PB84-149160

Source Receptor Methodology for Some Chlorinated Hydrocarbons

SRI International, Menlo Park, CA

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

Jan 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-149160

EPA-600/3-84-023
January 1984

SOURCE RECEPTOR METHODOLOGY FOR SOME CHLORINATED HYDROCARBONS

by

F. L. Ludwig, E. M. Liston and L. J. Salas
Atmospheric Science Center
SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

Contract No. 68-02-3416

Project Officer

James L. Cheney
Emissions Measurement and Characterization Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/3-84-023		PB84 149160

4. TITLE AND SUBTITLE	5. REPORT DATE
SOURCE RECEPTOR METHODOLOGY FOR SOME CHLORINATED HYDROCARBONS	January 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
F.L. Ludwig, E. M. Liston and L.J. Salas	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
SRL International 333 Ravenswood Avenue Menlo Park, California 94025	C9TA1B/01 - 0672 (FY - 83)
	11. CONTRACT/GRANT NO.
	Contract 68-02-3416
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Sciences Research Laboratory-RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	Final
	14. SPONSORING AGENCY CODE
	EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A source-receptor methodology is described that can be used to estimate emission rates of halogenated hydrocarbons from a manufacturing plant when access to the plant is not possible. An inert tracer is released at a known rate from a vehicle traveling back and forth on a road outside the plant area. Samples are collected downwind of the plant (at a distance of about 1 to 5 km) and analyzed for the tracer and the materials of interest. The relationship between the emission rates of the tracer and the measured concentrations has been derived. The method is generally insensitive to meteorological conditions, if applied at night or under overcast conditions during the day. It is suitable for estimating fugitive emisssions from sources within 10 or 15 m of ground level. It must be applied with discretion, if interfering sources are present in the area. Once emission rates have been determined, conventional Gaussian methods may be used to estimate expected maximum ground-level concentrations of the materials of interest downwind of the source area. A suitable manufacturing plant was selected (Vulcan Materials Company near Wichita, Kansas) and the method was applied to estimate emission rates for four different halogenated hydrocarbons. The feasibility of the methodology was demonstrated and suggestions for improvements were made.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	76
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

A source-receptor methodology is described that can be used to estimate emission rates of halogenated hydrocarbons from a manufacturing plant when access to the plant is not possible. An inert tracer is released at a known rate from a vehicle traveling back and forth on a road outside the plant area. Samples are collected downwind of the plant (at a distance of about 1 to 5 km) and analyzed for the tracer and the materials of interest. The relationship between the emission rates of the tracer and the materials of interest, and the measured concentrations has been derived. The method is generally insensitive to meteorological conditions, if applied at night or under overcast conditions during the day. It is suitable for estimating fugitive emissions from sources within 10 or 15 m of ground level. It must be applied with discretion, if interfering sources are present in the area. Once emission rates have been determined, conventional Gaussian methods may be used to estimate expected maximum ground-level concentrations of the materials of interest downwind of the source area. A suitable manufacturing plant was selected (Vulcan Materials Company near Wichita, Kansas) and the method was applied to estimate emission rates for four different halogenated hydrocarbons. The feasibility of the methodology was demonstrated and suggestions for improvements were made.

CONTENTS

Abstract iii
Figures vi
Tables vii

1. Introduction 1
2. Theory 5
3. Test Site 11
   Criteria used to select the test site 11
   Candidate test sites 12
   Test site--the Vulcan materials company, Wichita, Kansas 14
4. Test Procedures 21
   General 21
   Meteorological observations 22
   Tracer release procedures 22
   Sample collection procedures 24
   Sample analysis procedures 25
5. Test Results 27
   General 27
   Test of 8-9 August 1981 27
   Test of 10-11 August 1981 30
   Test of 11-12 August 1981 36
   Test of 12-13 August 1981 43
6. Interpretation of Results 49
   General approach 49
   Estimated emission rates 50
7. Summary and Recommendations 63
   Estimated emissions 63
   Suggested improvements in the methodology 63

References 67

FIGURES

Number		Page
1	Topographic map of the Vulcan plant site	15
2	Aerial photograph of the area surrounding the Vulcan plant	16
3	The perchloroethylene and chloromethane units at the Vulcan plant	17
4	The Vulcan plant viewed from the north	17
5	Aerial photograph of the Vulcan plant	19
6	Sampling locations and tracer release line for the night of 8-9 August 1981	29
7	Sampling locations and tracer release line for the night of 10-11 August 1981	35
8	Sampling locations and tracer release line for the night of 11-12 August 1981	40
9	Sampling locations and tracer release line for the night of 12-13 August 1981	45
10	Concentrations on 11 August 1981, 0000-0100 CST	51
11	Concentrations on 11 August 1981, 0100-0200 CST	53
12	Concentrations on 11 August 1981, 2200-2300 CST	55
13	Concentrations on 11 August 1981, 2300-2400 CST	58
14	Concentrations on 13 August 1981, 0400-0500 CST	60

TABLES

Number		Page
1	Suggested Values for the Constants in Equation (2)	6
2	Values of B for Typical Experimental Conditions	9
3	Producers of Chlorinated Hydrocarbons	13
4	SF_6 Release Data	23
5	Concentration of Reference Standards	26
6	Observed Weather Conditions in Wichita Area, 8-9 August 1981	28
7	Measured Concentrations, 8-9 August 1981	31
8	Observed Weather Conditions in Wichita Area, 10-11 August 1981	34
9	Measured Concentrations, 10-11 August 1981	37
10	Observed Weather Conditions in Wichita Area, 11-12 August 1981	39
11	Measured Concentrations, 11-12 August 1981	41
12	Observed Weather Conditions in Wichita Area, 12-13 August 1981	44
13	Measured Concentrations, 12-13 August 1981	46
14	Emission Rate Estimates for 11 August 1981, 0000-0100 CST	52
15	Emission Rate Estimates for 11 August 1981, 0100-0200 CST	54
16	Emission Rate Estimates for 11 August 1981, 2200-2300 CST	56

Number		Page
17	Emission Rate Estimates for 12 August 1981, 2300-2400 CST	59
18	Emission Rate Estimates for 13 August 1981, 0400-0500 CST	61
19	Summary of Emission Rate Estimates for Vulcan Plant	64

SECTION 1

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is concerned that some hydrocarbon compounds, especially halogenated hydrocarbon compounds that may be hazardous at low concentrations, might have an immediate local impact downwind of the plants that manufacture them. However, there has been a lack of data that would allow the prediction of either the amounts of these materials that are released to the atmosphere or the concentrations that might exist downwind of the plants under various meteorological conditions.

Several factors have contributed to this lack of data. First, these compounds do not come from clearly identified sources such as stacks or vents. Instead, they are likely to come from more widely distributed sources such as leaks from valves, plumbing, incompletely sealed containers, and filling and emptying operations, or during transport from one place to another. The magnitude of sources of this type is extremely difficult to measure or even estimate. The second, and almost equally important, reason why so few data are available concerning the magnitude of sources of halogenated hydrocarbons is that the processes and equipment used to produce the materials are frequently proprietary. Similarly, the manufacturers are quite secretive, for competitive reasons, about their production and sales rates. In such an environment, it is not surprising that the manufacturers are very reluctant to allow outsiders on the grounds of the manufacturing plants to make measurements that would be necessary to characterize source strengths directly.

The major problem has been just such a determination of source strengths. Once a source strength is known, maximum ground-level concentrations can be estimated as a function of downwind distance and meteorological conditions. The EPA recognized a need for a source-receptor methodology that could be used to estimate source strength and to predict maximum ground-level concentrations, and, for the reasons cited above, required that the method not rely upon measurements made within the manufacturing complex. Originally, measurements in the study described in this report were to be made within some manufacturing plant and used to verify the performance of a different methodology that required only measurments from outside the manufacturing area. The original intent of the study described in this report was to meet the following objectives:

(1) Select a suitable manufacturing site that produces two of the three following chlorinated hydrocarbons: methylene chloride (CH_2Cl_2), trichloroethylene (C_2HCl_3), and perchloroethylene (C_2Cl_4).

(2) Perform the necessary tests in the plant to establish the total fugitive emission rates of these compounds.

(3) Develop sampling strategies for fence-line and downwind measurements of the ambient concentration of these compounds.

(4) Develop a diffusion/transport methodology to predict the source strength and the downwind concentration from the fence-line measurements.

(5) Verify the model using source strengths estimated from the in-plant measurements.

(6) Develop a strategy for the use of the measurement methodology.

Four of the objectives were met. Objectives 2 and 5 were not achieved, because no suitable plant was found that would allow on-site measurements. Nevertheless, the project yielded a methodology that can be used to estimate the fugitive emissions from within a plant when access to the plant is not possible. The source-receptor methodology does not use measurements made literally at the fence line, unless the fence is sufficiently far from the sources that mixing will have produced reasonably uniform distributions through the lowest 10 m or so. This report describes that methodology and its application to a specific manufacturing plant. Suggestions are also included for improving the method and its application.

The theory underlying the methodology is discussed in the Section 2 of this report. Briefly, the methodology relies upon the release of an inert, nontoxic tracer gas at a known rate outside the manufacturing site. Concentrations of the tracer are measured downwind of the site to establish the magnitude of the atmospheric transport and dilution processes. This value is used in turn with simultaneous downwind measurements of the concentrations of the chlorinated hydrocarbons, allowing an estimate to be made of the magnitude of their sources within the plant. Once these source strengths have been established, conventional dispersion modeling techniques can be used to estimate downwind concentrations for various meteorological situations.

This report also describes the application of the methodology to a specific site and illustrates some of the important features of the method. The description begins with the selection of a candidate test site, followed by a discussion of the various parts of the test procedure:

(1) The requirements for meteorological observations

(2) The procedures used for tracer releases

(3) The procedures used for collecting and analyzing tracer samples.

(4) The procedures used for collecting and analyzing chlorinated hydrocarbon compounds.

Tests were conducted at the Vulcan Meterials Company plant near Wichita, Kansas, on the nights of 8-9, 10-11, 11-12 and 12-13 August 1981. This report describes the conditions that prevailed during these tests and interprets the results that were obtained to provide estimates of source emissions rates for some chlorinated hydrocarbons. The report concludes with a review of the methodology and a summary of the results obtained in the test application.

SECTION 2

THEORY

The theory underlying the source-receptor methodology used in this study is presented below. The derivation provides a relationship between the dilution of a tracer released from a ground-level line source and the dilution of materials released from a nearby ground-level area or point source. First, consider the Gaussian formula for a ground-level concentration from an infinite ground-level line source:

$$C_1 = \frac{2Q_1}{\sin\Phi u\ \sigma_z \sqrt{2\pi}} \qquad (1)$$

where

C_1 = ground-level concentration (g m^{-3})

Q_1 = line-source emission rate (g $m^{-1}s^{-1}$)

Φ = angle between wind and line source

u = windspeed (m s^{-1})

σ_z = standard deviation of Gaussian concentration distribution in the vertical at a distance from the source parallel to the wind direction (m).

The vertical standard deviation σ_z can be approximated by a function of the following form:

$$\sigma_z(x) = ax^b \qquad (2)$$

where x is the distance from the source, parallel to the wind direction. Table 1 gives values of a and b suggested by Busse and Zimmerman (1) for use in the range from about 0.5 to 5 km downwind.

If we substitute from Eq. (2), Eq. (1) becomes:

$$C_1 = \frac{2Q_1}{\sin\Phi \sqrt{2\pi} u a x^b} \qquad (3)$$

TABLE 1. SUGGESTED VALUES FOR THE CONSTANTS IN EQUATION (2)

Atmospheric Stability	Constants	
	a	b
Extremely unstable	0.25×10^{-3}	2.09
Moderately unstable	0.049	1.11
Slightly unstable	0.10	0.93
Neutral (day)	0.26	0.69
Neutral (night)	0.25	0.63
Stable	0.20	0.60

SOURCE: Busse and Zimmerman (1)

The formula for an area source (of infinite extent in the cross-wind direction) can be obtained by integrating Eq. (3) along x:

$$C_A = \frac{2Q_A\left(X_u^{1-b} - X_d^{1-b}\right)}{\sin\Phi\sqrt{2\pi}\ Ua(1-b)} \quad \text{for } b \neq 1 \tag{4}$$

where X_u and X_d are the distances to the upwind and downwind edges of the area source and Q_A (g m^{-2} s^{-1}) is the area-source emission rate. The "line sources" that are integrated to get Eq. (4) can be oriented arbitrarily. For convenience, we choose to orient them at the same angle to the wind Φ as the tracer line source. Dividing Eq. (4) by Eq. (3) gives

$$\frac{C_A}{C_1} = \frac{Q_A\left(X_u^{1-b} - X_d^{1-b}\right) \cdot x^b}{Q_1(1-b)} \tag{5}$$

Solving for Q_A gives:

$$Q_A = \frac{C_A Q_1}{C_1} \frac{(1-b)}{\left(X_u^{1-b} - X_d^{1-b}\right) \cdot x^b} \tag{6}$$

All quantities on the right side of Eq. (6) can be measured experimentally except b, which depends on atmospheric stability. For experiments conducted at night, the atmosphere will be either stable or neutral according to the commonly used methods for classifying atmospheric stability (2). If we limit the downwind distances at which measurements are made so that x, X_u and X_d are all between 0.5 and 5 km, then the appropriate values of b range from about 0.6 for stable conditions to about 0.7 for neutral conditions (1).

Although a value based on meteorological factors can be chosen for b, there is some uncertainty, so it is important to evaluate the sensitivity of the relationship to the choice of value for b. We begin by defining a factor containing all the b terms as follows:

$$B = \frac{1-b}{\left(X_u^{1-b} - X_d^{1-b}\right) \cdot x^b} \cdot \tag{7}$$

Substituting Eq. (7) in Eq. (6) gives:

$$Q_A = \left(\frac{C_A Q_1}{C_1}\right) B \qquad (8)$$

Table 2 gives values of B for b = 0.6 and b = 0.7, by using different combinations of x, X_u, and X_d. It is apparent from the table that the calculations are not very sensitive to atmospheric stability. Within the limits of experimental accuracy, b could be set equal to 0.65, and Eq. (6) would then become:

$$(Q_A)_{night} \approx \frac{0.35 C_A Q_1}{C_1 \left(X_u^{0.35} - X_d^{0.35}\right) x^{0.65}} \qquad (9)$$

Some assumptions inherent in Eq. (9) should be understood:

(1) Eq. (9) applies for nighttime conditions or neutral daytime atmospheric conditions.

(2) Concentrations are measured 0.5 to 5 km downwind of the sources.

(3) Concentrations are measured near the center of the plume where the assumption of an infinite crosswind extent of the sources is most nearly valid.

(4) The crosswind extent of the sources is large compared to the dimensions of a point-source plume at the downwind distance where the concentrations are measured, e.g.,

- At 5 km, about 600 m for neutral stability and about 300 m for stable.
- At 2 km, about 300 m for neutral and about 150 m for stable.

(5) The angle between the wind and the line source is relatively large, about 45° or greater.

(6) The separation between the line source and the area source should be kept as small as possible, preferably within about 25% of the distance between the line source and the samplers.

In general, the above conditions that apply to the line source were met, except for the requirement that the wind direction be at a large angle to the line source. This was not met for the night test of 8-9 August 1981. This test, and the test of 7-8 August 1981, were only marginal with regard to the crosswind extent of the area from which fugitive emissions were expected. From the standpoint of meeting the

TABLE 2. VALUES OF B FOR TYPICAL EXPERIMENTAL CONDITIONS

x (m)	X_u (m)	X_d (m)	B (m^{-1})		Relative Difference (%)
			b = 0.6	b = 0.7	
4000	4400	4200	$5{\cdot}22 \times 10^{-3}$	$5{\cdot}26 \times 10^{-3}$	0.7
4000	3800	3600	$4{\cdot}77 \times 10^{-3}$	$4{\cdot}74 \times 10^{-3}$	0.8
2000	2400	2200	$5{\cdot}44 \times 10^{-3}$	$5{\cdot}51 \times 10^{-3}$	1.3
2000	1800	1600	$4{\cdot}53 \times 10^{-3}$	$4{\cdot}46 \times 10^{-3}$	1.6
1500	1900	1700	$5{\cdot}57 \times 10^{-3}$	$5{\cdot}68 \times 10^{-3}$	2.0
1500	1300	1100	$4{\cdot}37 \times 10^{-3}$	$4{\cdot}27 \times 10^{-3}$	2.3

assumptions underlying Eq. (9), the last three tests were the best. The data analyses presented later focus on these three cases.

It is also possible to assume that the plant emissions come from a point or very small area at the surface, with a source strength Q_p. The concentration at the center of the plume (C_p) is given by:

$$C_p = \frac{Q_p}{\pi U \sigma_y \sigma_z} \quad , \tag{10}$$

where σ_y is the standard deviation of the Gaussian concentration distribution in the crosswind direction; σ_y is approximately proportional to $X_p^{0.9}$ (2). The constant of proportionality depends on stability. It ranges from 0.065 for moderately stable atmospheric conditions to 0.13 for neutral conditions, when both X_p and σ_y are expressed in the same units (m); X_p is the downwind distance from the point source.

If the point source and the line source are close together compared to the downwind distance, then $(X_p/X)^b \approx 1$ for the values of b discussed earlier. For example, if $0.85 \leq (X_p/X) \leq 1.15$, then $(X_p/X)^b$ will be between about 0.9 and 1.1. Using this fact, we can determine the ratio between Eqs. (1) and (10), and solve for Q_p to give:

$$Q_p = K \frac{C_p}{C_l} Q_l \frac{X_p^{0.9}}{\sin\phi} \quad , \tag{11}$$

where

$$K = \begin{cases} 0.32 & \text{for a neutral atmosphere} \\ 0.25 & \text{for a slightly stable atmosphere} \\ 0.16 & \text{for a moderately stable atmosphere} \end{cases}$$

Eq. (11) is not quite as desirable as Eq. (9) for estimating source strength because it is subject to appreciable dependence on atmospheric stability. However, it does not require an estimate of the size of the area source in order to determine total emission rates. In the analyses that follow both Eqs. (9) and (11) have been used.

SECTION 3

THE TEST SITE

The EPA wanted this study to be performed at a site that manufactured two of the three following chlorinated hydrocarbons: methylene chloride (CH_2Cl_2), trichloroethylene (C_2HCl_3), and perchloroethylene (C_2Cl_4). There are only a limited number of such manufacturing sites in the United States; a list of these sites was compiled and each site was evaluated according to the criteria discussed below.

CRITERIA USED TO SELECT THE TEST SITE

Although it was not emphasized in the preceding section, it is essential to be able to establish that measured concentrations of the halocarbons of interest come from the plant in question. Therefore, the area surrounding the manufacturing site must be free of other sources of the same materials. Such sources would interfere with interpretation of the data and make it difficult to estimate source strengths within the plant itself. Therefore, one of the criteria for selecting the test site was that there be no other nearby sources of chlorinated hydrocarbons.

The use of a tracer to estimate dilution rates requires that the tracer be released as close to the sources of interest as possible. It also requires that samples of ambient air be collected or measured both upwind and downwind of the manufacturing site, preferably within a few kilometers of the site. Inasmuch as the wind can blow from any direction, it is desirable to have the area around the plant be accessible for a few kilometers in every direction. A flat, open terrain with many lightly traveled roads is most desirable.

The tracer methodology is most appropriately applied at night. Therefore, a plant that operates on an around-the-clock schedule is desirable so that the tests can be conducted at night when winds are light and the air is stable. This criterion was not very restrictive in the site selection process, because all the plants that were considered do operate on such a schedule. Nevertheless, it must be considered.

The diffusion/transport methodology assumes that most emissions occur near ground level and that mixing through the lower layers is about the same as that of the tracer. The methodology would not be applicable to a plant where appreciable quantities of the materials are emitted from tall stacks. This criterion was not restrictive for the plants considered in the selection process, because virtually all the emissions at these plants take place within 5 to 10 m of the surface and with little

buoyancy. When questioned, the manufacturers stated that all stack gases are processed through incinerators before venting, so there should be no emissions from the stacks.

The final criterion used for selecting a test site was that the manufacturer be cooperative and allow access to the plant. This particular criterion proved impossible to satisfy. Although most of the manufacturers were willing to discuss the planned tests and to consider allowing access to the plant, none was actually willing to grant such access. The reasons for their unwillingness, which were cited in Section 1, are certainly valid from their perspectives. It should also be noted that the operator of the plant that was finally selected for this study was cooperative enough to furnish some information on plant products and operations.

CANDIDATE TEST SITES

Only seven plants in the United States produce the chlorinated hydrocarbons of interest. These are listed in Table 3. The table also identifies which of the compounds are produced at each of the sites. The operators of these plants were contacted, maps of the areas surrounding the plants were obtained, and climatological data for the regions were studied during the selection process. Initially, SRI believed that one or more of the operating companies might be willing to allow access to their plants, or that the EPA could expeditously negotiate access on our behalf. Under the assumption that access could be obtained, SRI focused on three particular plants, which were visited. These plants were PPG Industries, Inc., Lake Charles, Louisiana; Stauffer Chemical Company, Louisville, Kentucky, and Vulcan Materials Company, Wichita, Kansas. The latter plant was finally chosen because it best met the selection criteria--other than the criterion regarding cooperation by the operator. This site will be discussed in detail in the next section.

The Louisville and Lake Charles sites were not selected because they would have been more difficult for field operations than the Wichita site. The marshy terrain surrounding the Lake Charles site limits the number of available roads in some directions from the plant. The Ohio River is next to the Louisville plant, so that extensive travel would have been required to get from the plant to some sampling areas. Although it would have been possible to conduct tests at the Louisville and Lake Charles sites, surroundings limited the number of wind directions under which tests could have been conducted and would have introduced some logistical problems that were not encountered at the Wichita site. Inasmuch as the purpose of the program was to develop and demonstrate the source-receptor methodology, it would have been counterproductive to introduce unnecessary complications.

There was another more serious reason for rejecting the Louisville site. It was not entirely clear that there were no other sources of

TABLE 3. PRODUCERS OF CHLORINATED HYDROCARBONS

Company and Location	Products		
	CH_2Cl_2	C_2HCl_3	C_2Cl_4
Dow Chemical Company, USA			
Freeport, TX	✓	✓	✓
Plaquemine, LA	✓	✓	
Ethyl Corporation			
Baton Rouge, LA		✓	✓
PPG Industries, Inc.			
Lake Charles, LA		✓	✓
Stauffer Chemical Company			
Louisville, KY	✓	✓	
Vulcan Materials Company			
Geismar, LA	✓	✓	
Wichita, KA	✓	✓	

chlorinated hydrocarbons in nearby industrial areas. This is also why the Dow Chemical plant at Freeport, Texas, and the PPG plant at Lake Charles, Louisiana, were not given serious consideration. The application of the methodology in an area of large-scale petrochemical production, such as Freeport, Texas, could pose some serious difficulties. SRI does not believe that applying the methodology in such areas would be impossible, but it would likely require careful selection of the conditions under which the tests were conducted and appreciably more measurements upwind of the plant to establish ambient background conditions. It would also require a careful analysis of land use and manufacturing operations in the region, and a more thorough interpretation of the collected data. It seemed premature to introduce these complications before the method had been demonstrated under more favorable conditions.

The reasons for rejecting the other plants listed in Table 3 were similar to those discussed above. Briefly, the Dow Chemical plant at Plaquemine, Louisiana, is located next to the Mississippi River, which would have posed serious logistical problems. The Vulcan plant at Geismar, Louisiana, and the Ethyl plant at Baton Rouge, Louisiana, were not given serious consideration because SRI had been refused entry earlier in the project. By the time it became evident that in-plant tests would not be possible, SRI had already selected the Vulcan plant at Wichita as the best site.

TEST SITE--THE VULCAN MATERIALS COMPANY, WICHITA, KANSAS

The Vulcan Materials Company plant was chosen as the site for testing the source-receptor methodology. The plant is located about 35 m southwest of the center of Wichita, Kansas. Figure 1 is a topographic map showing the area near the plant site. The area around the plant is quite flat; within 2 km of the plant, the elevation changes over a range of less than 15 m (about 1,280 to 1,320 feet). The site is serviced by a railroad, which also serves a grain elevator about 1 km to the northeast. A wastewater treatment plant and a fluorocarbon manufacturing plant (both operated by Vulcan) are adjacent to the Vulcan site and a power plant is located about 2 km to the northeast. A small chemical plant is located about 0.3 km south of the Vulcan site, but it does not use any of the materials of interest.

Other than these activities, the area surrounding the Vulcan plant is generally devoted to farming for at least 5 km in all directions. As the map shows, there is a grid of roads at 1.6-km intervals around the plant, but these are generally not heavily traveled, especially during the night and early morning hours when the tests were conducted. Figure 2 is an aerial photograph (taken February 1977 by the Kansas Gas and Electric Co.) of the immediate vicinity of the plant. Figures 3 and 4 are ground-level photographs of the plant that were taken during this project. Figure 3 shows the "perchloroethylene" unit (produces perchloroethylene and carbon tetrachloride) on the left and the "chloromethane" unit (produces methylene chloride, chloroform, and carbon tetrachloride) on the right. Figure 4 shows the plant and the surrounding farmland.

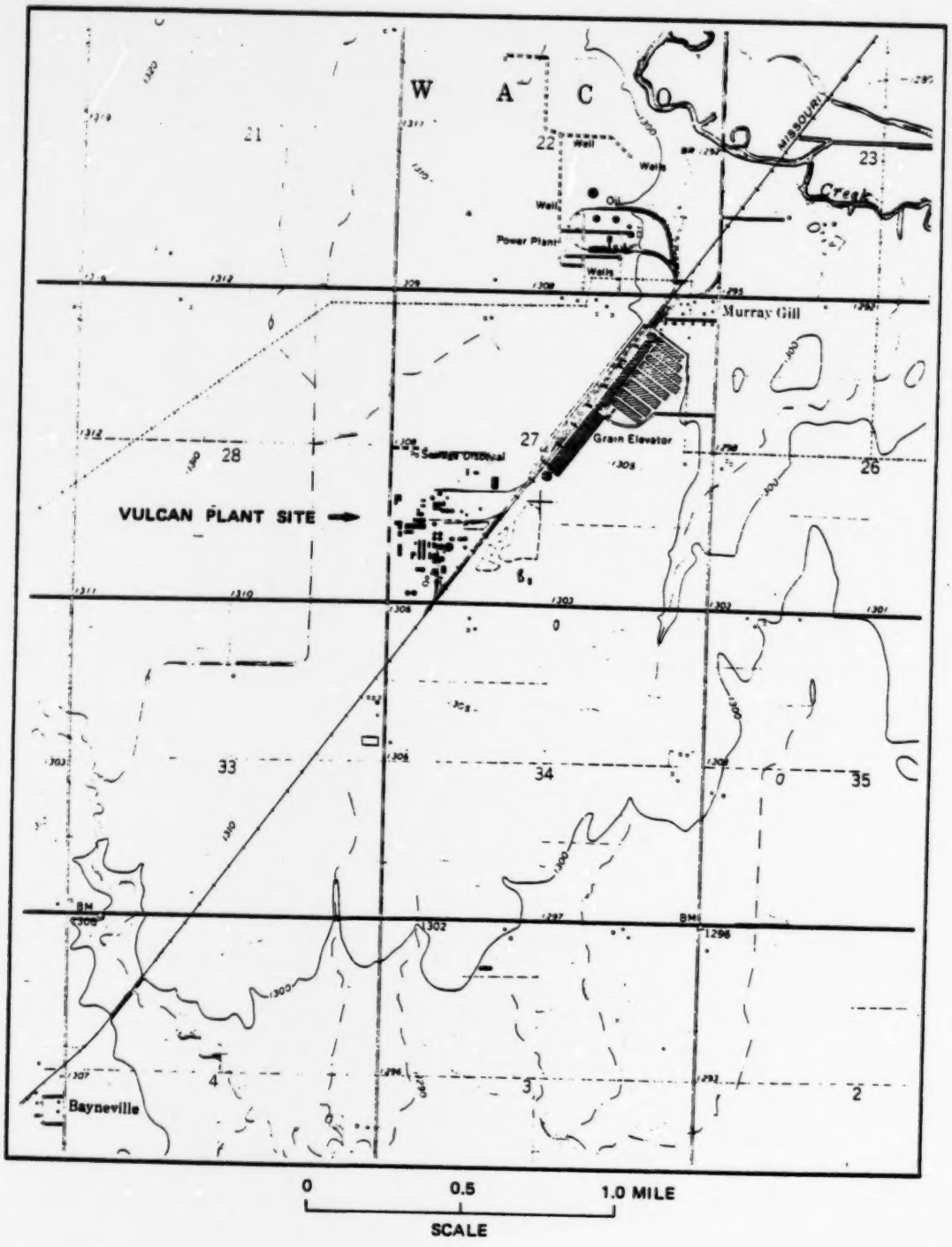

Figure 1. Topographic map of the Vulcan plant site.

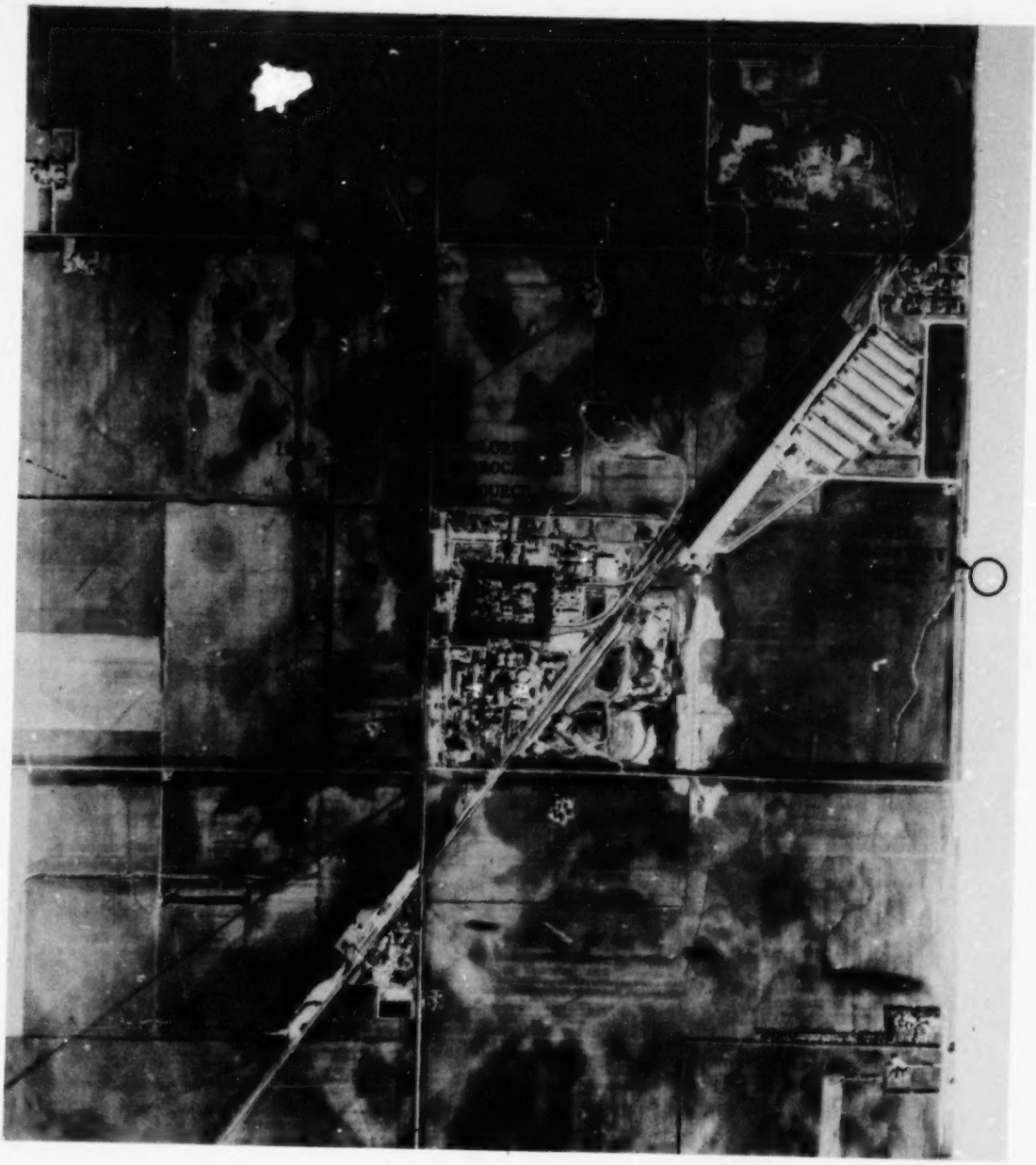

Figure 2. Aerial photograph of the area surrounding the Vulcan plant. (Photograph provided by Kansas Gas and Electric Company.)

Figure 3. The perchloroethylene and chloromethane units at the Vulcan plant.

Figure 4. The Vulcan plant viewed from the north.

The Vulcan plant is a medium-sized plant occupying a retangular space approximately 500 m in the east-west direction and 600 m in the north-south direction. However the area involved in solvent operations is much smaller. Figure 5, a section of the aerial photograph shown in Figure 2, indicates areas where operations might be conducted that would be related to the emissions of the solvents of concern. The outside boundaries of these sources are approximately 225 m in the east-west direction and 150 m in the north-south direction, but emissions of any given material are not likely to be present at all locations within these boundaries. Later, for the purpose of estimating the total emissions, it is assumed that the total emitting area is about 25,000 m^2; this is about 60% of the solvent area described above. As noted earlier, it is believed that the emissions are all likely to occur within 5 to 10 m of the surface and at ambient temperatures, so there is not likely to be any significant buoyant rise.

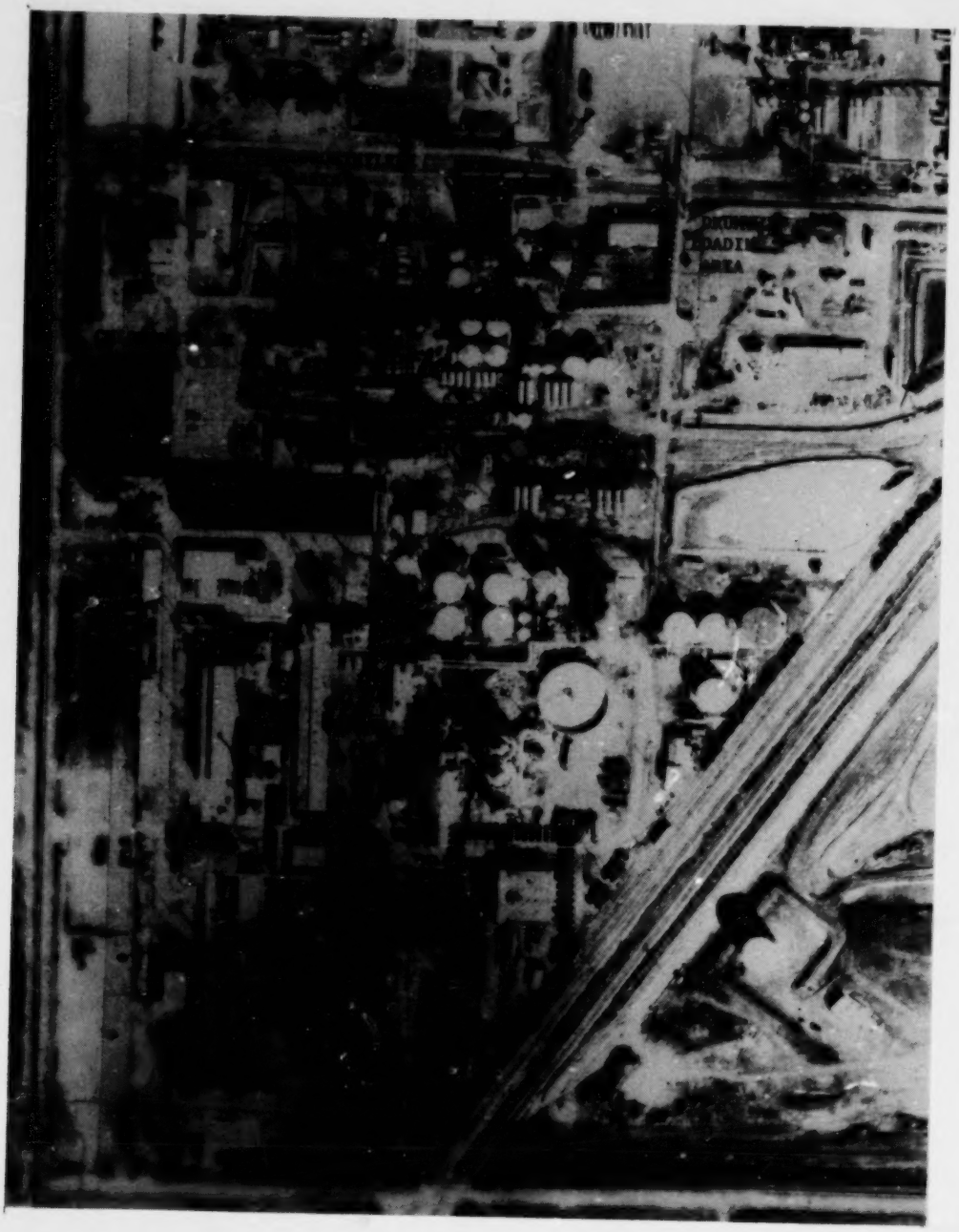

Figure 5. Aerial photograph of the Vulcan plant. (Photograph provided by Kansas Gas and Electric Company.)

SECTION 4

TEST PROCEDURES

GENERAL

This section describes the test procedures that were applied at the Vulcan manufacturing site near Wichita, Kansas. These procedures would generally apply for all sites. The need to collect samples upwind and downwind of the plant, as well as the methods for collecting and analyzing these samples would not change. The theory underlying the source-receptor methodology dictates that the best results will be obtained during the nighttime hours, because the method is not particularly sensitive to prevailing meteorological conditions when the atmosphere is stable, as it often is at night. The theory also dictates that the tracer releases be made in a line that is as close to the manufacturing plant as possible and as nearly perpendicular to the wind direction as possible.

Several considerations suggest that the sample collection be done as near the source as possible. Concentrations should be higher near the source; hence, the results of the chemical analysis should be more reliable. Collecting the samples near the source should also minimize the lateral spreading effects that negate the assumption of an infinite line source, which was used in deriving some of the equations for the methodology. However, one very important factor dictates that the samples not be collected too close to the source. The theory presumes that both the tracer and the materials of interest are released at approximately the same low altitude. Vertical mixing will tend to minimize the effects of differences in the release heights of the various materials at distances of 1 km or more from the source, where the vertical spread--as measured by the vertical standard deviation, σ_z, of a Gaussian concentration distribution--should be at least 15 m, even under moderately stable conditions. This would be enough to provide a reasonably uniform concentration distribution (when averaged over about an hour) through the lowest 10 to 20 m of the atmosphere for materials that have been released within that same layer. As noted earlier, the assumption of an infinite line source makes it desirable to minimize the lateral spreading. During nighttime conditions, the lateral spread--as measured by the horizontal standard deviation, σ_y, of a Gaussian distribution from a point source--will generally be 200 m or less to downwind distances of about 3 km. Therefore, the downwind samples should usually be collected at distances between 1 and 3 km downwind.

METEOROLOGICAL OBSERVATIONS

One of the reasons for developing a methodology based on the release of a tracer gas was to minimize the need for meteorological observations. Conventional, easily made meteorological observations are not directly related to all the factors that affect the diffusion and transport of emissions released from a plant. The relationship between conventional measurements and atmospheric stability is particularly subject to uncertainties. Nevertheless, there are operational requirements for some meteorological observations when using the tracer technique. Futhermore, meteorological observations provide an important source of backup information as well as information that can be used to interpret concentration data.

Most important to both the data interpretation and operational planning of the study are windspeed and wind direction observations. These were measured at an altitude of about 10 m in the immediate vicinity of the test site. The measurements were made with a propeller-vane anemometer at SRI's mobile laboratory site, indicated in Figure 2. The temperature and humidity were also measured at the same site, at a height of about 5 m.

In addition, SRI obtained copies of the official hourly weather observations made by the U.S. National Weather Service at Mid-Continent Airport in Wichita, Kansas, about 8 km north of the test area. These observations included temperature, humidity, windspeed and wind direction, and visual estimates of cloud amount and type. Airport wind directions represent more or less instantaneous measurements, subjectively averaged over about a minute or two, while those at the site were averaged over the hour, beginning at the time shown in the table. Cloud amount and type are important to the estimation of atmospheric stability class.

TRACER RELEASE PROCEDURES

The tracer chosen for this study was sulfur hexafloride (SF_6), commonly used because it is totally inert and nontoxic, and because it occurs only at very low concentrations in the atmosphere. The tracer was released from the back of a moving vehicle through a flow-limiting needle valve. The use of a flow-limiting valve ensured a relatively constant emission rate. The flow rate was measured at nominal half-hour intervals using a Singer Model 115, dry test meter. Flow rates were very constant (±3%) over an 8-hour period. The total emissions during a test were determined from the weight of the SF_6 cylinder before and after the test. The average emission rate was determined from the following relationship:

$$\overline{Q}_1 = \frac{W}{Lt} \quad ,$$

where

$\bar{Q}_1$ = the average line-source emission rate of SF_6 ($g\ m^{-1}s^{-1}$)

W = the total weight of SF_6 released, as determined by weighing (g)

L = the length of the road segment over which the vehicle drove while releasing SF_6 (m)

t = the time interval over which the SF_6 release took place (s).

It is possible to use an average emission rate, determined as described above, for these tests because the samples that are collected are also averaged over extended periods of time (1 h). If the averages obtained this way are to be reasonable approximations of the true average, the release vehicle must traverse the road segment at least six or seven times per hour. (In the experiments reported, it was traversed approximately 40 times per hour.)

There is the tacit (and reasonable) assumption that the meteorological conditions are uncorrelated with the location of the release vehicle.

For all of the test data considered in this report, a segment of road approximately 0.82 km in length was used. This road is immediately west of the plant, approximately 225 m from the center of the hydrocarbon manufacturing area (see Figure 2). It was possible to make quick U-turns at the intersections at each end of the road segment, because traffic was light during night hours on the road. Because the U-turns could be made quickly, it was not necessary to turn off the tracer release at these times. The release vehicle generally traveled about 32 km h^{-1} while traversing the road segment, so about 40 passes over the segment could be made during each hour.

Table 4 lists the release data for each night's testing.

TABLE 4. SF_6 RELEASE DATA

Date of Test	Release Path Length (m)	Average Speed m/s	Passes per Hour	Total Release Rate (g/hr)	Line Release Rate (μg/m s)
8/8 - 8/9	815	8.9	40	839	290
8/10 - 8/11	815	9.1	40.2	988	336
8/11 - 8/12	815	8.9	39.2	900	308
8/12 - 8/13	815	9.7	40	918	291

SAMPLE COLLECTION PROCEDURES

Bag Samplers

The downwind samples were taken at ground level by using the automatic samplers that SRI routinely uses for this type of work. These samplers manufactured by Environmental Measurements Inc. (EMI), are multiple-bag samplers containing 12 pumps and an electronic timing circuit by which up to 12 1-hour bag samples can be obtained sequentially. The EMI sampler is approximately 60 cm in diameter and 110 cm high, and weighs 11 kg. The sampler is operable over a temperature range of -10^{o} to 50^{o} C.

Each sampler is battery operated and uses a timing circuit that actuates the pumps intermittently to conserve battery life. The start time for sequential sampling (for the night operation) can be set in advance on each timer. As a result, it was possible to service the samplers in advance, before they were placed at the sampling sites in the early evening.

The EMI samplers were initially designed to actuate the pumps on a duty cycle of 2 s on and 30 s off to produce a 5-liter sample each hour. The timing circuits on a set of these samplers owned by SRI have been modified to obtain a duty cycle of 80 ms on and 1 s off. In addition, the bag size has been reduced to 2 L. These modifications provide a more representative hourly sample than can be obtained with the factory-supplied pump duty cycle, while still providing more than adequate sample volume.

From our experience with these samplers, SRI has found that Tedlar is the best material for these bags. It has no background of chlorinated hydrocarbons and it has very low permeability, so samples can be stored without contamination or loss. The bags are fabricated at SRI and a large number of them were in stock for use in the study. The bags were routinely checked for leakage during the test program. SRI has developed a routine bag cleaning process that was used between each sampling. The cleaned bags were tested on a random basis to ensure that they had been cleaned properly and that there was no inadvertent contamination. Each of the bags was identified with a label listing the sampler number and the time that the sample started.

Sample Locations

The samplers were placed at ground level, at power poles whenever possible. They were chained to the poles for security. For the first three tests, the samplers were placed at approximately 300-meter intervals. For the last test, the spacing was decreased to approximately 150 m, because a preliminary review of the data indicated that the plume might be passing between samplers.

The arc covered by the samplers was dictated by the wind direction and the prediction of wind direction from the U.S. National Weather Service. The sampler locations are shown on the maps presented in Section 5.

The samplers were placed at the designated locations by 2200 CST, and they were collected the following morning, beginning at 0700. After the samplers were returned to the mobile laboratory site, the bags were removed, checked for proper inflation, and hung in special racks pending analysis. Bags from the previous night's run were cleaned and used to reload the samplers.

SAMPLE ANALYSIS PROCEDURES

Chlorinated Hydrocarbons

The samples were analyzed using two Perkin-Elmer Model 3920 gas chromatographs (GCs), each with dual columns, injectors, and detectors. Each GC was equipped with a 1-meter injection loop, which was cooled with liquid oxygen to trap the halocarbons from 50-cm^3 gas samples. It was then heated with boiling water to transfer the concentrated sample into the GC. The columns were 10 ft x 1/8 in (304 x 0.32 cm) 80/100 mesh SP2100. They were operated isothermally at 50° C with a total analysis time of 20 min.

Tracer Gas

SF_6 analysis was performed using a System Science and Software Model 215 AVP Environmeter, which is an electron-capture GC that operates at ambient temperatures. This GC uses an internal vacuum pump to flush and fill a 2-cm^3 gas sampling loop, which is valved to introduce the samples. The output of the electron capture detector is sensed by an electrometer circuit, which is coupled to a peak read-and-hold circuit for digital peak maximum display, and a buffer amplifier that drives the analog output. In the test, the analog output was connected to a Hewlett-Packard Model 3390A computing integrator, which automatically labeled the sample, the peak elution time, and the peak area. The only modification used from the standard production model was the addition of a Brooks flow controller to allow finer control of the carrier gas flow rate.

Calibration

Calibration standard gases (Scott-Marin) were diluted with ultra-high purity nitrogen to make a series of calibration gases for the chlorinated hydrocarbons. In addition, there was a series of six prediluted standards for SF_6. The concentrations of these standards are given in Table 5.

Data Reduction

A data acquisition system was connected to the output of the GC. This system was designed to actively record the elution time and area of each peak. The peak area was then used to calculate the concentration of the species. During the test program, an intermittent failure occurred in the data acquisition system, causing it to record incorrect areas for some of the peaks. This failure was not discovered until

detailed data analysis was performed. For those cases where an incorrect area was recorded, SRI attempted to estimate the area from peak height. This was only partially successful, so any data based on peak height are considered unreliable.

The GC analyses provided measurements of CCl_4 concentrations, as well as those for the other three compounds. Although not required by the contract, results based on the CCl_4 measurements are presented in the following sections.

TABLE 5. CONCENTRATION OF REFERENCE STANDARDS

Gas	Concentration
C_2HCl_3	1.2 ppb
C_2Cl_4	1.2 ppb
$C_2H_3Cl_3$	1.25 ppb
CCl_4	1.3 ppb
SF_6	25.6 ± 5 ppt
	55.7 ± 5 ppt
	105 ± 5 ppt
	511 ± 5 ppt
	1050 ± 50 ppt
	10600 ± 500 ppt

SECTION 5

TEST RESULTS

GENERAL

This section describes the conduct of the four successful tests and the concentrations observed during those tests. An interpretation of these observations will be presented in Section 6, along with dilution ratios and inferred emission rates. In this section, each of the four tests is presented separately, beginning with an overview of the meteorological conditions that prevailed during the test and followed by a description of the tracer release and the sampling array. Any information about samplers that were moved during the evening to better measure the patterns that were expected from the observed wind direction is also included. Finally, the observed concentrations for each test are tabulated.

TEST OF 8-9 AUGUST 1981

Meteorological Conditions

Table 6 summarizes the prevailing meteorological conditions during this test. It can be seen that the skies were clear until about 0500 CST on the morning of 9 August 1981. The temperature fell, in response to radiative cooling under clear skies. Winds tended to be light, generally less than 3 m s^{-1} at the site and at the airport. The winds were blowing from directions between about 200° and 250° (approximately from south-southwest to west-southwest). Light winds and cloudless skies generally accompany stable atmospheric conditions, so it is reasonable to assume that the atmosphere was stable during this evening.

Test Operations

Figure 6 shows the locations where samples were collected during this test. With winds generally blowing from the southwest, the samplers were located northeast of the plant. The road segment over which the SF_6 releases took place is also shown in Figure 6. With a southwest wind, it was not possible to find a road segment that was normal to the wind. The data collected on this evening were not as useful as those collected on some of the other evenings, because of the location of the line-source tracer release relative to wind directions.

TABLE 6. OBSERVED WEATHER CONDITIONS IN WICHITA AREA, 8-9 AUGUST 1981

Hour (CST)	Sky Cover (tenths)	Wind				Temperature (°F)	Relative Humidity (%)
		At Site		Mid-Continent Airport			
		Direction (°)	Speed (ms^{-1})	Direction (°)	Speed (ms^{-1})		
2100	0			150	2.1	74	66
2200	0			200	1.5	73	66
2300	0			190	2.6	71	68
2400	0	200	1.8	210	2.1	72	64
0100	0	210	2.7	230	2.1	69	68
0200	0	210	2.7	230	2.1	68	68
0300	0	220	3.1	250	2.6	67	70
0400	0	210	2.7	240	2.1	67	70
0500	2	200	1.8	---	0	64	78

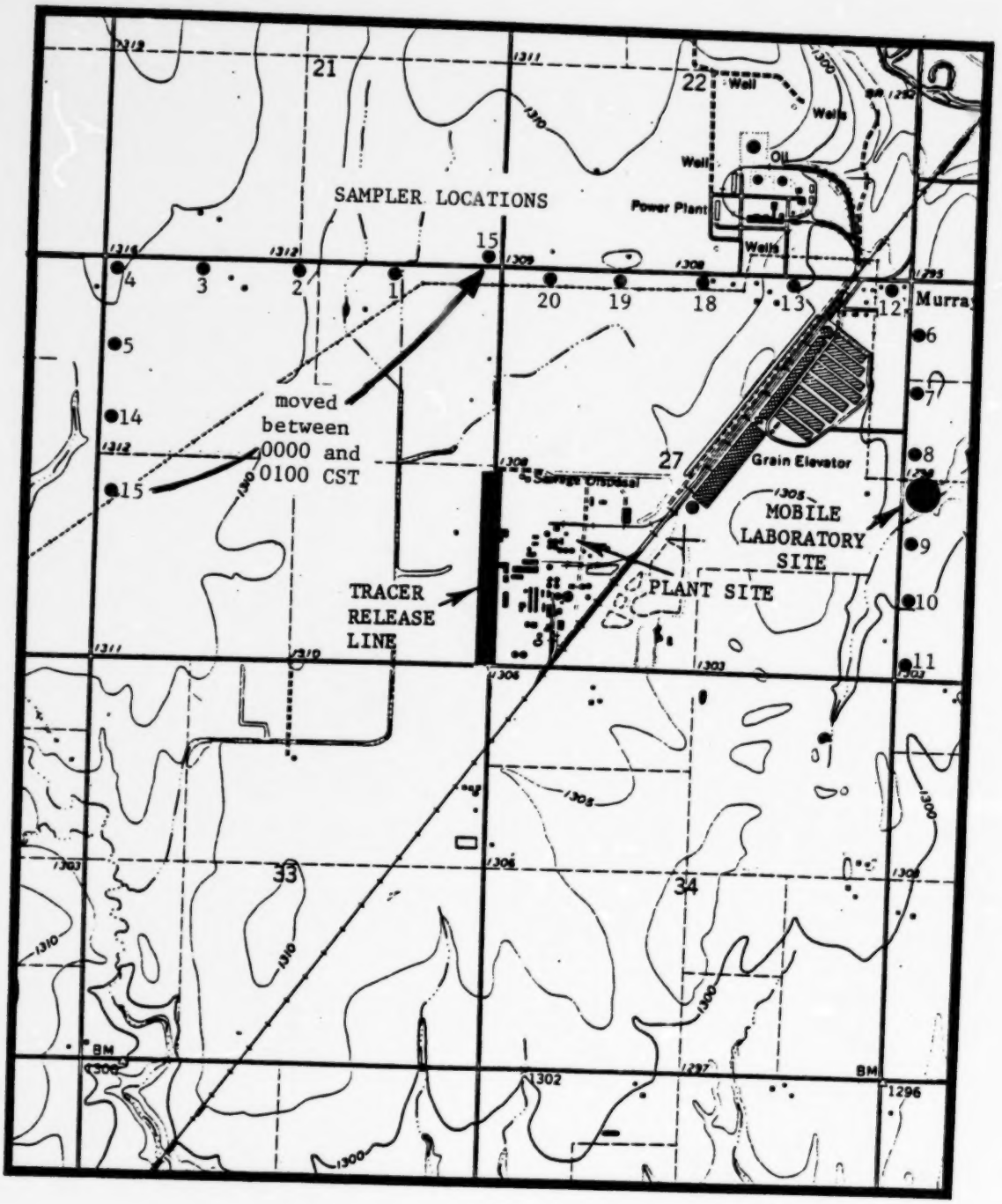

Figure 6. Sampling locations and tracer release line for the night of 8-9 August 1981.

Observed Concentrations

Table 7 summarizes the concentrations of the tracer and the chlorinated hydrocarbons that were measured. The sampling locations refer to those marked in Figure 6. It should be noted that some of the samplers were moved during the course of the test in order to provide an arc that was more nearly centered on the downwind direction. Complete analyses were not performed on samples for which the SF_6 results indicated little effect from the plant area.

The concentrations varied considerably from one location to another and from one time period to another. This high degree of variability is frequently observed; it appears to reflect a corresponding variability in the emissions from the plant. The importance of this variability to the design and execution of future experiments will be discussed later. Although none of the data collected during this evening were suitable for estimating the emission rates, they do indicate the concentration levels that are observed in the vicinity of the plant.

TEST OF 10-11 AUGUST 1981

Meteorological Conditions

Table 8 summarizes the meteorological conditions during this test. As was the case during the 8-9 August test, the winds were light, generally less than about 2 m s^{-1} at the site. (They were slightly stronger at the airport.) Wind directions and sky conditions differed considerably from those of 8-9 August. Winds were initially from the east-southeast, but around midnight they switched to north-northeast. Overcast skies accompanied this wind shift. Initially, the overcast was altocumulus at about 3,000 m. Later, a layer of cirrostratus was observed at about 7,500 m. The cirrostratus overcast was dense enough to be considered opaque by the observer. Overcast skies are generally accompanied by neutral stability (2).

Test Operations

The location of the samplers and the route over which the line-source tracer release was made are shown in Figure 7. Initially, when the wind direction was from the east, a line of samplers was placed west of the site, as shown in the figure. However, as the wind developed a more northerly component, it was deemed necessary to add samplers south of the plant. Thus, samplers were installed and operated after about 0115 CST at the locations marked 19, 20, 1, and 2. Unfortunately, these samplers were faulty, and the samples collected could not be used. It would probably have been wise to realign the tracer release route at about the same time that the additional samplers were placed. This would have provided a line-source release that was more nearly perpendicular to the wind direction during the later hours.

TABLE 7. MEASURED CONCENTRATIONS, 8-9 AUGUST 1981[a]

Compound	Hour (CST)	Sampling Location[b]									
		2	1	15	20	19	18	13	12	6	7
CCl_4	2000	F[c]		1.72	.98	1.20[d]	2.03[d]	.97	12.0	3.08[d]	.95[d]
	2100	F		2.23	3.06	5.83	4.94[d]	20.5	3.71	5.32[d]	1.97[d]
	2200	6.28		8.65	9.21	.81[d]	F		2.19	2.03[d]	2.20[d]
	2300	4.4	3.42	.97	164.0	.74[d]	3.62[d]	1.64	3.43	1.39[d]	.65[d]
	0000	0.43	3.71	.75	15.6	4.12	2.54[d]	8.72	.38[d]	1.30[d]	.30
	0100	2.69[d]	3.28	.35	.90	8.47	F	15.3	1.75[d]	1.77[d]	3.13[d]
	0200	.296[d]	3.13	1.01	F	4.77[d]	F	69.2	1.44[d]	3.62[d]	2.54[d]
	0300	.327[d]	2.67	.72	F	1.14[d]	.47[d]	183.0	12.0	11.8[d]	1.85
	0400	.325[d]	9.86	.88		.67[d]	F		11.5	7.11[d]	
	0500	3.76			1.91	1.22[d]	6.10[d]	186.0	11.3	F	.57[d]
	0600			4.10			F	15.1	1.08	1.43[d]	1.03
SF_6	2000		.09	.14	.13	.16	13.7	.16	.07	.17	.11
	2100			.05	.58	.09	.15	.06	.04	.09	.05
	2200	2.61		.81	2.64	.11	F		.11	.09	.20
	2300	.05	.10	.02	1.57	.02	.04	.02	.01	.03	6.26
	0000	.09	.08	.02	5.87	.02	.03	.02	.02	.05	.52
	0100	.04	.10	.16	6.92	12.7	F	.06	.02	.04	.19
	0200	.02	.15	.61	F	9.35	F	.93	.05	.01	1.66
	0300	.01	.10	.06	F	9.57	9.70	4.05	1.78	.48	.10
	0400	.03	19.4	.03	5.87	8.35	F	2.39	1.07		
	0500	.04			12.3	19.0	5.96	1.51	.23		.11
	0600			14.5			F	.03	.02	.07	.59

See footnotes at end of table.

(continued)

TABLE 7 (continued)

Compound	Hour (CST)	Sampling Location[b]									
		2	1	15	20	19	18	13	12	6	7
C_2HCl_3	2000	F		4.67	4.65	4.50[d]	16.9[d]	9.57	5.56	26.1[d]	5.64[d]
	2100	F		2.02	5.13	1.45[d]	3.62[d]	3.92	10.1	10.5[d]	2.79
	2200	16.3		9.57	4.75		F		6.76	6.50[d]	10.2[d]
	2300	1.37[d]	1.91	6.53	2.05	1.67[d]		6.98	2.06[d]	13.2[d]	1.69
	0000	1.82	1.57	10.8	5.22	2.77[d]	1.97[d]	5.26	.88	4.42[d]	1.34[d]
	0100	1.34[d]	1.73	2.62	3.56	1.37[d]	F	5.33	1.20	5.94[d]	4.72[d]
	0200	1.25[d]	1.76[d]	6.58	F	1.52[d]	F	2.53	1.40	7.00[d]	4.33[d]
	0300	1.17[d]	1.99	8.23	F	1.52[d]	6.61[d]	2.80	1.83	9.63[d]	6.57
	0400	1.54[d]	5.18	4.00		1.07[d]	F		2.82	6.33[d]	
	0500				3.56	1.25[d]	4.75[d]	2.93	1.25[d]	F	8.32[d]
	0600			27.6			F	3.04	10.5	9.52[d]	5.24
C_2Cl_4	2000			2.04	2.02	.44[d]	2.48[d]	1.58	3.16	18.7[d]	10.4
	2100			1.26	2.75	.48[d]	2.17[d]	1.35	21.8	5.36[d]	1.67
	2200	24.0		2.84	1.94	.00[d]	F		4.63	4.53[d]	3.56[d]
	2300	.35[d]	.95	4.63	4.75	1.03[d]	1.38[d]	1.62	.60[d]	7.14[d]	.43
	0000	.35[d]	.58	1.22[d]	2.14	.48[d]	1.01[d]	1.75	.44[d]	.32[d]	.79[d]
	0100	.31[d]	.56	1.03	1.58	.89[d]	F	1.46	.67	4.02[d]	2.57[d]
	0200	.31[d]	.66	1.67	F	.74[d]	F	3.14	.48	5.05[d]	2.20[d]
	0300	.31	.91	2.69	F	.33	2.48[d]	23.7	2.02	18.2[d]	4.18
	0400	.31[d]	1.06	1.17		.35[d]	F		1.14	10.8[d]	
	0500	.31			1.27	.37[d]	3.10[d]	15.6	1.57[d]		.41[d]
	0600			45.2			F	1.35	4.84	2.40[d]	2.46

See footnotes at end of table.

(continued)

TABLE 7 (continued)

Compound	Hour (CST)	Sampling Location[b]									
		2	1	15	20	19	18	13	12	6	7
$C_2H_3Cl_3$	2000			7.76	1.36	328.0[d]	10.8[d]	7.21	6.97	10.7[d]	5.0[d]
	2100			6.65	7.93	9.24	9.26[d]	.41	5.97	9.76	5.53[d]
	2200	11.1		14.2	5.19	$(4.03)10^6$[d]	F		9.26	10.1	10.6[d]
	2300	13.5	13.3	5.36	.41	36200.0[d]	10.6[d]	5.79	14.0	13.6[d]	5.49[d]
	0000	2.99	4.10	4.75	6.51	9.72	6.16[d]	4.67	6.0	8.83[d]	5.73[d]
	0100	3.89[d]	3.19	3.65	9.29	10.9	F	21.9	3.18	9.95[d]	10.0[d]
	0200	3.53[d]	.34[d]	6.27	F	3.30[d]	F	4.14	5.03	10.4[d]	9.76[d]
	0300	4.69[d]	3.27	11.1	F	12.7	12.7[d]	5.37	6.17	9.85[d]	7.27
	0400	4.51[d]	6.35	4.72		11.9			10.7	9.46[d]	
	0500	11.3			11.4	13.4	11.6[d]	8.18	12.1		4.09[d]
	0600			8.95			F	5.12	9.59	10.6	9.14[d]

[a]Concentrations expressed in $\mu g\ m^{-3}$.

[b]See Figure 6 for sampling locations.

[c]F = flat bag.

[d]Peak height measurements.

TABLE 8. OBSERVED WEATHER CONDITIONS IN WICHITA AREA, 10-11 AUGUST 1981

Hour (CST)	Sky Cover (tenths)	Wind				Temperature (°F)	Relative Humidity (%)
		At Site		Mid-Continent Airport			
		Direction (°)	Speed (ms^{-1})	Direction (°)	Speed (ms^{-1})		
2200	1	70	1.8	100	2.1	69	73
2300	7	100	1.8	110	2.1	69	73
2400	10	85	1.3	40	2.6	69	73
0100	10	45	0.4	360	1.5	69	76
0200	10	30	0.9	20	2.1	68	79
0300	10	30	0.9	350	2.1	66	84
0400	10	20	0.9	40	2.1	66	84
0500	8	15	0.9	30	2.6	65	84
0600	9	20	0.9	--	0	64	84

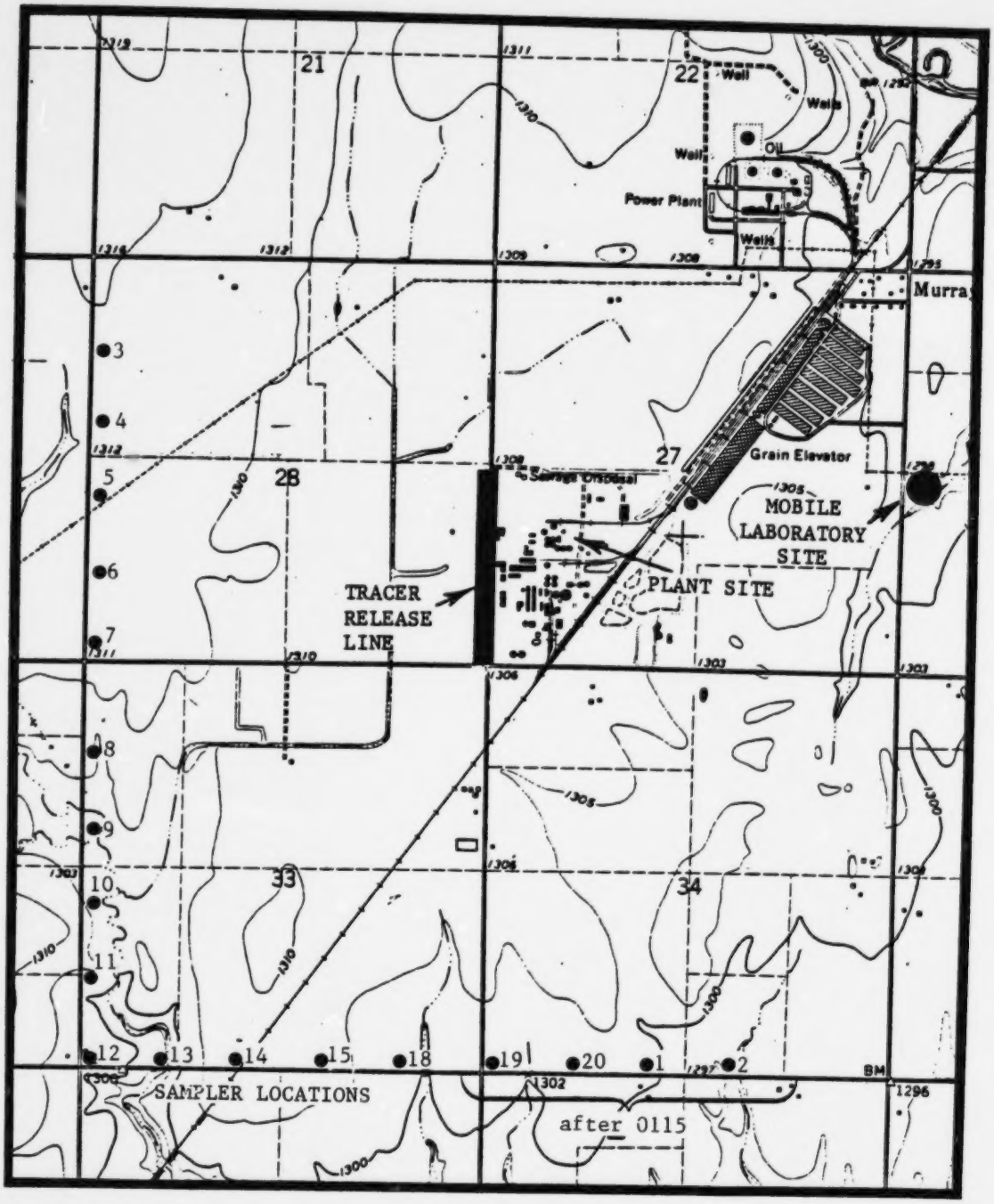

Figure 7. Sampling locations and tracer release line for the night of 10-11 August 1981.

Observed Concentrations

Table 9 gives the observed concentrations of the tracer and the chlorinated hydrocarbons. As shown in Table 8, the winds between 2400 and 0100 at the site were generally from the east (85°) and shifted to the northeast during the following hour. The data collected during these 2 h show significant concentrations of CCl_4 and C_2HCl_3. It appears that there may have been above-normal releases of material that were detected by the sampling network during this period. For that reason, 2 h have been chosen for interpretation and for estimating the release rates. They will be discussed in greater detail in the next section.

TEST OF 11-12 AUGUST 1981

Meteorological Conditions

The meteorological conditions that prevailed during this test are summarized in Table 10. The skies were overcast during most of the period, so the atmospheric stability was neutral. Winds at the site were generally from the east until about 0300, when they shifted to the southeast. Winds were from the east at the Mid-Continent Airport until about midnight, when they shifted to southerly; later, the winds were more from the southeast. During the last 3 h of the test period, the airport winds were approximately south-southeast. Table 10 shows that the temperature dropped about 3° F during this period. Relative humidity rose correspondingly from 64 to 78%. The cloud cover throughout this period was cirrostratus at an altitude of about 7,500 m.

Test Operations

Figure 8 shows the sampler locations and the route traveled during the tracer release operations. The sampling array was set up to accomodate the winds at the beginning of the period. These winds were from the east or slightly northeast, so the array was quite suitable for measuring influences from the tracer line and from the plant. However, around 0400 CST, the winds shifted, so most of the materials were carried north of the sampling line.

Observed Concentrations

Table 11 gives the concentrations of the various materials. As noted earlier, the wind directions during the first few hours of this period were nearly perpendicular to the roadway on which the tracer was released. This is the most suitable alignment for application of the method described earlier. One of the test hours (2200-2300 CST) has provided interesting data that could be used to estimate emissions from the plant.

TABLE 9. MEASURED CONCENTRATIONS, 10-11 AUGUST 1981[a]

Compound	Hour (CST)	Sampling location[b] 18	15	14	13	12	11	10	9	8	7	6	5	4	3
SF_5	2200	1.32		.21		.01		.06		F[c]	.05	.04	.05		.07
	2300	.05			.01	.01		.02			1.38	F[c]	.20	.03	.05
	0000	3.56		.18	.03	.01		.01			.61	1.11	2.25	.20	.04
	0100	.10	.03	.07				.27			.05	.05	.04	F[c]	.08
	0200	.10	.03	.02		.07					.06	.06	.06	F[c]	F[c]
	0300	.10	.03	.13	.03			.02			2.44	.07	.04	.04	.01
	0400	.06			.16	.04		F[c]			.51		.07	F[c]	F[c]
	0500	.20		.15		.02		.01			.04	.05	.07	.03	.05
	0600		.03	.01	.14		.01	.04			.07	.07	.06	.02	.03
CCl_4	2200			7.17	.51[d]	54.4	193	23.2	51.6		1.52[d]				.15
	2300	1.39[d]	.91[d]	4.51	1.19[d]	.39	3.65	.66[d]	10.5	154	7.31[d]			3.89	.13
	0000	1.59	.65[d]	6.18	.23[d]	.29	12.3	4.26	2.46	13.8	4.45[d]	5.25	2.69	3.31	.33
	0100	1.20		25.9	4.41[d]	6.7	22.2	.45[d]	1.01	6.08	1.73[d]				.63
	0200	5.47[d]		.79[d]	.72[d]	.45	7.27	.69[d]			1.25[d]				
	0300	1.16[d]			1.16[d]	.09		.72[d]			1.53[d]				.50
	0400	2.12[d]			1.78[d]	.99					1.84[d]				
	0500	4.17		.66	1.09[d]	.21		.55[d]			1.41[d]				.95
	0600			.51[d]	1.10[d]	.21		3.60			1.18[d]				.57
C_2HCl_3	2200	12.0[d]		8.92	1.79[d]	8.04	8.95	1.95[d]	5.06		3.28[d]				1.46[d]
	2300	26.7	1.42[d]	5.33	4.64[d]	2.61	3.59	2.77[d]	10.4	8.42	12.9[d]			2.02	2.85[d]
	0000	20.3	0.2[d]	15.8	2.68[d]	18.4	10.5	5.66	22.1	16.5	22.4[d]	26.7	3.79	32.8	8.69[d]
	0100	17.2		8.72	14.3[d]	26.5	13.5	8.04[d]	28.0	12.7	13.6[d]				16.4
	0200	19.3[d]		5.00[d]	5.08[d]	17.2	5.26	4.50			10.4[d]				
	0300	2.79[d]			4.75[d]	15.4		5.64[d]			9.69[d]				2.90[d]
	0400	3.58[d]			8.46[d]	10.8					3.93[d]				
	0500	4.84		5.79	1.79[d]	6.53		2.15[d]			3.64[d]				2.74[d]
	0600			1.43[d]	5.71[d]	9.65		22.1			4.30[d]				4.50

See footnotes at end of table.

(continued)

TABLE 9 (continued)

Compound	Hour (CST)	Sampling Location[b] 18	15	14	13	12	11	10	9	8	7	6	5	4	3
C_2Cl_4	2200	1.88		1.61	.39[d]	2.32	5.12	.87	1.68		2.02[d]				.31
	2300		.48[d]	1.50	1.80[d]	3.86	.18	.52[d]	2.50	4.29	3.18[d]			1.57	.68[d]
	0000	2.42	.44[d]	1.65	.22[d]	2.04	1.76	.48[d]	1.67	3.01	2.48[d]	3.85		1.70	.48
	0100	2.89		2.12	2.04[d]	3.25	1.76	.52[d]	2.08	1.48	2.09[d]				3.07
	0200	2.75[d]		.74	.64	2.45	2.05	.40[d]			1.82[d]				
	0300	.55			.78	2.93		.15			1.74[d]				.48
	0400	1.35[d]			2.29[d]	2.08					1.74[d]				
	0500	1.55[d]		1.40	.49	2.20		.26[d]			1.10[d]				1.19
	0600			.44[d]	1.01[d]	1.86		.09			1.21[d]				.98
$C_2H_3Cl_3$	2200			5.20	3.43[d]	8.39	6.10	10.0[d]	3.31		7.34[d]				6.09[d]
	2300		11.6[d]	6.29	9.04[d]	19.8	.93	7.14[d]	9.58	6.90	9.46[d]			5.54	5.94[d]
	0000	4.76	4.34[d]	7.79	8.12[d]	9.81	9.39	7.03[d]	7.54	5.99	9.35[d]	9.38	5.05	8.57	3.10
	0100	5.69		6.37	7.12[d]	8.34	8.52	5.30[d]	9.44	7.84	8.77[d]				7.94
	0200	6.92[d]		6.30[d]	11.6	8.77	8.71	7.18[d]			8.61[d]				
	0300	5.04			6.14[d]	8.66		13.1			8.70[d]				8.09[d]
	0400	.55[d]			9.05[d]	8.58					8.34[d]				
	0500	6.92[d]		6.01	10.1	8.43		5.10[d]			8.67[d]				
	0600			4.08[d]	7.25[d]	5.93					8.49[d]				7.06

[a]Concentrations expressed in μg m^{-3}.

[b]See Figure 7 for sampling locations.

[c]F = flat bag.

[d]Peak height measurement.

TABLE 10. OBSERVED WEATHER CONDITIONS IN WICHITA AREA, 11-12 AUGUST 1981

Hour (CST)	Sky Cover (tenths	Wind				Temperature (^{o}F)	Relative Humidity (%)
		At Site		Mid-Continent Airport			
		Direction (^{o})	Speed (ms^{-1})	Direction (^{o})	Speed (ms^{-1})		
2100	10	80	2.2	70	3.1	72	64
2200	10	90	1.8	80	2.6	71	66
2300	10	100	1.8	90	3.1	70	68
2400	10	110	1.3	190	1.5	67	78
0100	10	90	0.4	140	1.5	67	73
0200	10	100	0.9	130	2.6	67	71
0300	10	95	0.9	130	2.1	65	78
0400	10	135	0.9	160	1.5	64	79
0500	8	155	0.9	160	1.5	64	78
0600	8	140	0.9	160	1.5	65	78

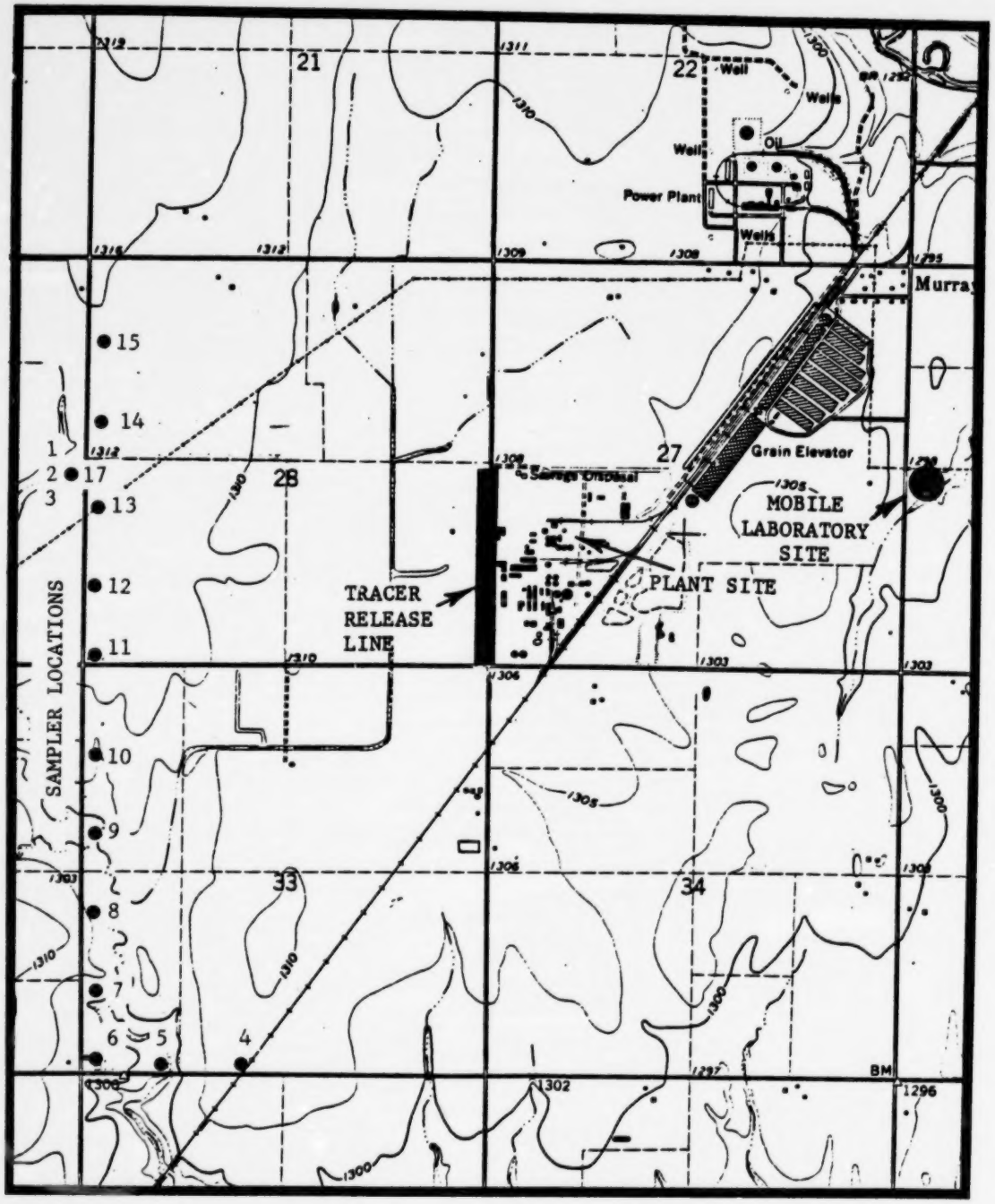

Figure 8. Sampling locations and tracer release line for the night of 11-12 August 1981.

TABLE 11. MEASURED CONCENTRATIONS, 11-12 AUGUST 1981[a]

Compound	Hour (CST)	Sampling Location[b] 5	6	7	8	9	10	11	12	13	3	17	14	15
SF_6	2200	.04	.06	.05		.04	.03	.10	.69	.13	.15	1.14	.14	.14
	2300	.03	.03	.05	.01	.04	.07	1.53	3.08	1.42	.52	.79	.57	.43
	0000	.30	.25	.06	.05	.04	.03	.39	1.17	1.60	3.47	1.35	1.39	F[c]
	0100	.88	.90	.03	.02	.04	.42	1.04	16.7	2.21	1.33	1.68	2.08	1.68
	0200	.05	.04	.02	.02	.09	.61	1.37	3.52	2.70	2.21	4.83	.83	.67
	0300	.03	.04	.02	.03	.07	.18	.60	5.74	2.98	2.88	F[c]	6.00	.33
	0400	.97	1.84	.03	.02	.26	.04	.05	.10	.83		3.61	1.54	12.9
	0500	.06	.11	.02	.04	.04	.04	.02	.11	.09	1.31	2.03	.88	.15
	0600	.78	2.32	.03	.13	.03	.05	.61	.13	.05	.81	1.97	.17	
CCl_4	2200	2.46[d]	14.8	1.15		1.66[d]	61.8	5.42[d]	44.7	6.92	.45[d]	.72	.63	2.05[d]
	2300	1.42[d]	9.36	.75		.23	39.8	1.32[d]	13.3	7.02	1.99[d]		12.0	1.06[d]
	0000	3.53[d]	10.6	.72	1.02	.58[d]	4.01	1.13[d]	33.7	9.06	9.31	17.7	51.1	
	0100		76.7	.50	.60	.50[d]	10.5	1.44[d]		11.0	7.27[d]	5.71[d]	28.0	8.23[d]
	0200	2.04[d]	7.12			.65[d]	4.87	1.84[d]	5.28	11.3	4.95	11.5	6.74	4.37[d]
	0300	1.60[d]	8.07	.92	.60	.47[d]	21.7	4.15[d]	15.9	9.81	10.0		243	4.51[d]
	0400	6.97[d]	153	1.03	.32	.58[d]	.81	1.37[d]	.82[d]	1.19		73.2	13.5	6.87[d]
	0500	1.70[d]	6.77		.86[d]	.57[d]	8.32	1.54[d]	1.40[d]	1.54	14.1	11.7[d]		1.39[d]
	0600	3.27[d]	188	.80	.86	.52[d]	140	1.65[d]	2.34	1.76	2.62[d]	.004[d]	.78[d]	
C_2HCl_3	2200	18.6[d]	23.3	37.3		12.2[d]	22.4	28.3[d]	18.9	6.11	8.69[d]	32.8	26.8	24.2[d]
	2300	5.60[d]	10.3	6.15		2.88[d]	3.44	6.66[d]	1.97[d]	1.61	7.99[d]	.03	9.16	7.90[d]
	0000	5.77[d]	3.57	9.90	9.90	2.35	6.32	6.78[d]	3.65	1.87[d]	4.22	52.0	5.49	
	0100		2.95	6.92[d]	6.85	2.36	8.15	7.50[d]		2.15[d]	3.66[d]	31.5[d]	4.22	5.60[d]
	0200	5.88[d]	5.45			2.46[d]	.52	3.76[d]	1.59[d]	1.70[d]	2.90[d]	49.7	5.08	5.60[d]
	0300	4.87[d]	5.33	5.83	5.99	1.16[d]	13.9	8.40[d]	3.27	1.41[d]	3.80[d]		9.26	4.93[d]
	0400	4.59[d]	2.83	6.62	7.36	2.77[d]	13.7	6.10[d]	2.11	2.69[d]		29.9	40.8	5.44[d]
	0500	4.68[d]	.67		9.90	1.97[d]	13.7	6.94[d]	5.38[d]	1.78[d]	3.24[d]	50.5	.53	3.94[d]
	0600	4.64[d]	3.17	6.44	8.91	2.96[d]	60.1	3.57[d]	2.04	1.63	3.49[d]	37.5[d]	67.7[d]	

See footnotes at end of table.

(continued)

TABLE 11 (continued)

Compound	Hour (CST)	Sampling Location[b]												
		5	6	7	8	9	10	11	12	13	3	17	14	15
C_2Cl_4	2200	1.88[d]	2.90	2.23		.92[d]	4.10	3.93[d]	2.05	.87[d]	.52[d]	2.78	2.10	1.93[d]
	2300	1.90[d]	4.04	1.85		.48[d]	1.26	1.29[d]	.81[d]	4.72	.65[d]	2.02[d]	6.13[d]	1.23[d]
	0000	1.72[d]	2.04	2.56	1.52	.35[d]	.67	1.09[d]	1.67	.33	.85	4.39	9.5[d]	
	0100		3.34	1.55	1.28	.29	2.35	1.47[d]		.49	.52[d]	3.61[d]	5.22	6.37[d]
	0200	1.35[d]	2.28			.31[d]	1.15	.68[d]	.61	2.34	.83[d]	3.96	2.74	2.03[d]
	0300	1.47[d]	1.71	1.34	1.74	.22[d]	1.36	1.83[d]	1.60	.06	.70[d]		11.8	1.38[d]
	0400	4.22[d]	7.15	2.77	1.34	.26[d]	1.06	1.28[d]	.43	.45		1.66	2.26	3.99[d]
	0500	1.09[d]	1.72		2.74	.35[d]	1.18	1.10[d]	1.37[d]	.37	.31	2.88	1.20	1.01[d]
	0600	1.11[d]	1.47	1.61	.97	.26[d]	1.12[d]	1.29[d]	.31	.31	.39[d]	2.00[d]	1.04[d]	
$C_2H_3Cl_3$	2200	5.63[d]	5.46	5.10		3.30[d]	5.05	5.19[d]	5.99	7.04	4.46	5.71[d]	5.51	8.90[d]
	2300	5.07[d]	5.56	4.21		2.15[d]	4.42	5.76[d]	14.8	2.62	2.93[d]	9.85	4.86	3.65[d]
	0000	5.86[d]	3.29	4.48	4.21	3.38	2.87	4.64[d]	5.63	18.1	3.91	6.54	11.0	
	0100	4.92[d]	4.63	3.57	3.87	3.20	7.64	6.18[d]		14.0	7.05	7.61[d]	5.61	9.11[d]
	0200	6.07[d]	5.24			3.60[d]	8.11	3.13[d]	3.49	5.31	4.16[d]	16.3	4.29	8.91[d]
	0300	4.86[d]	4.91	3.61	3.08	2.79	11.3	8.43[d]	5.78	16.6	7.53		8.16	5.06[d]
	0400	6.30[d]	4.14	4.00	3.80	3.76[d]	5.25	12.2[d]	6.55	3.35[d]		.90	4.56	6.26[d]
	0500	5.97[d]	3.42		5.65	11.2	4.67	8.73[d]	10.4[d]	14.6	4.45			4.91[d]
	0600	6.66[d]	4.65	3.94	4.79	8.25[d]	8.38[d]	8.90[d]	12.9	3.61[d]	3.39[d]	6.79[d]	4.85[d]	

[a]Concentrations expressed in $\mu g\ m^{-3}$.

[b]See Figure 8 for sampling locations.

[c]F = flat bag.

[d]Peak height measurement.

TEST OF 12-13 AUGUST 1981

Meteorological Conditions

Table 12 summarizes the observed weather conditions for 12-13 August 1981. This was another overcast night, but the clouds were lower on this night than on the preceding two nights. The overcast was altostratus at altitudes of a few thousand meters. During the earlier part of the period, there was light drizzle; a 2-hour period of light rain turned to drizzle at about 2015 CST. Because of the rain and the heavy overcast, temperatures remained nearly constant throughout the period, and the humidity was consistently high.

The winds during this night were generally from the south and south-southeast, usually within 30° of a south wind. The windspeeds were light, but somewhat stronger than on the other nights, exceeding 4 m s^{-1} by 0600 CST.

Test Operations

Figure 9 shows the location of the samplers used during this test. It should be noted that the selection of these sampling locations was based on the southeast winds that prevailed at the beginning of the test. As the winds became more southerly at later hours, this array proved to be less than ideally located. As the winds became more southerly, they also became more nearly parallel to the tracer release line shown in the figure. This was a poor choice of tracer release route. A better choice would have been along the east-west road to the south of the plant.

Observed Concentrations

Table 13 summarizes the observed concentrations at various locations on this night. Two of the hours during the period, when winds were at a greater angle to the tracer release line, were suitable for analysis and for estimating the emission rates.

TABLE 12. OBSERVED WEATHER CONDITIONS IN WICHITA AREA, 12-13 AUGUST 1981

Hour (CST)	Sky Cover (tenths)	Wind				Temperature (°F)	Relative Humidity (%)	Remarks
		At Site		Mid-Continent Airport				
		Direction (°)	Speed (ms^{-1})	Direction (°)	Speed (ms^{-1})			
2100	10	150	2.2	160	3.1	72	84	Light drizzle
2200	10	160	1.3	160	2.6	72	84	
2300	10	160	1.3	150	2.1	72	84	
2400	10	175	1.3	170	3.1	72	84	
0100	10	170	1.3	180	3.1	71	87	
0200	10	170	1.8	170	3.1	71	87	
0300	10	160	1.8	150	3.1	71	87	
0400	10	150	2.2	170	3.6	71	84	
0500	10	160	2.7	170	3.6	71	84	light rain
0600	10	160	4.0	160	4.6	71	87	light shower, fog

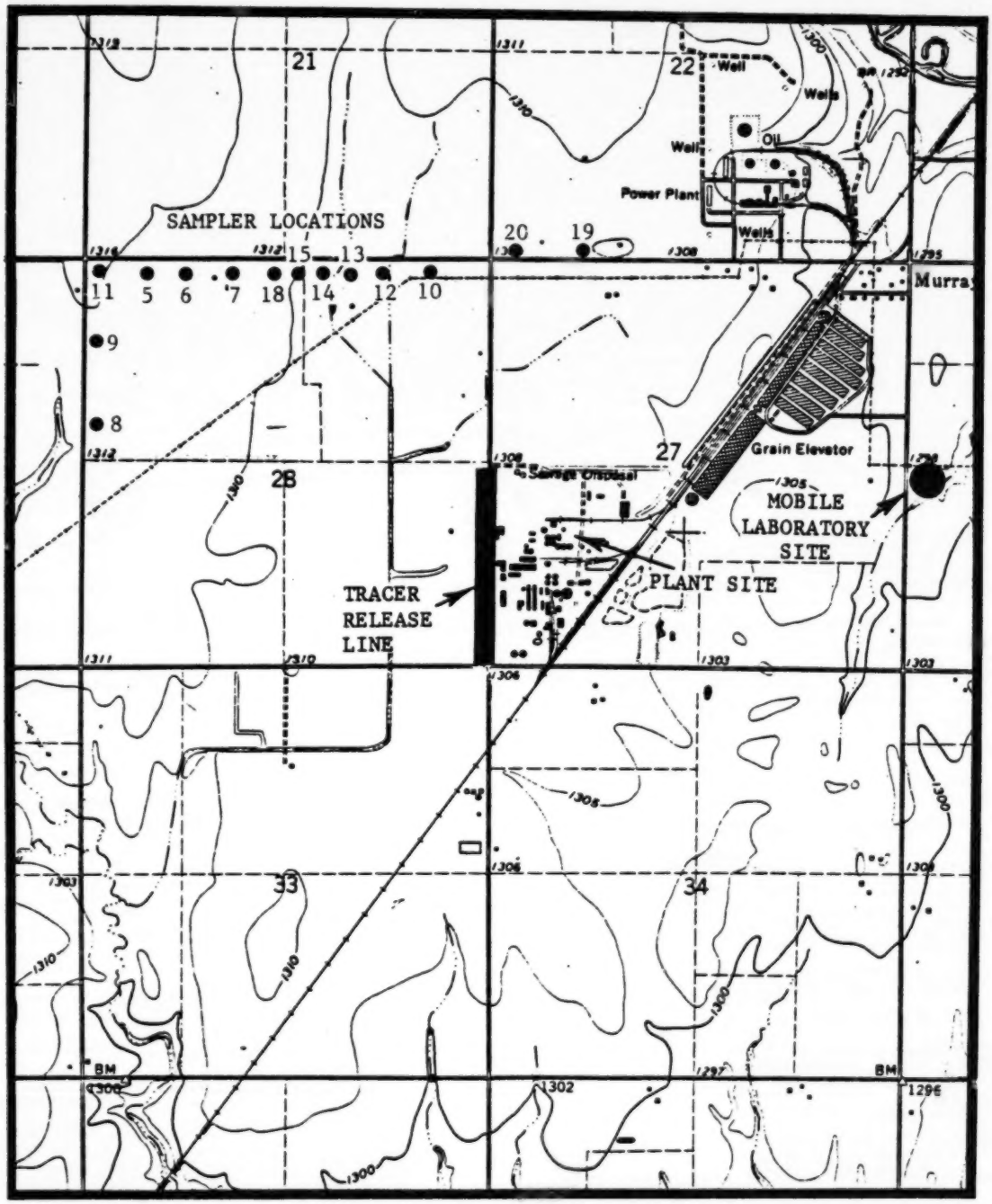

Figure 9. Sampling locations and tracer release line for the night of 12-13 August 1981.

TABLE 13. MEASURED CONCENTRATIONS, 12-13 AUGUST 1981[a]

Compound	Hour (CST)	Sampling Location[b]													
		8	9	11	5	6	7	18	15	14	13	12	10	20	19
SF_6	2200	.66	.82	.60	F	.40	.82	2.37	1.51	1.80	.52	.30	3.63		
	2300	.04	.04	.14	.78[d]	1.59	18.4	1.13	F[c]	1.32	2.06	1.71	1.57	.71	28.9
	0000	1.12	37.6	.84	F[c]	.31	.77	5.44	.98	.92	3.39	.73	4.48	7.31	.38
	0100	27.4	8.05		43.5[d]	.07	3.26	1.14	F[c]	7.79	6.44	6.87	3.43	2.09	1.13
	0200	.02	.23	.23	.21	24.4	0,1	1.76	1.73	2.82	2.93	4.31	3.02	1.02	1.17
	0300	15.5	.28	28.2	2.06	1.46	1.63	2.28	1.60	F	20.7		1.37		.06
	0400	.05	.55	3.87	3.25	11.5	2.51	2.46	3.59	2.89	.29	1.92	.11	.08	.15
	0500	.03	26.0	.66	1.41	1.42	2.31	4.70	2.05	5.22	.73	.15	.25		.73
CCl_4	2200	1.13		13.7	F[c]	5.66[d]	9.16	3.86	74.7	6.00[d]	3.15[d]	4.07	3.75[d]		
	2300	1.45	.59[d]	7.52	.84[d]	1.51[d]	23.3	1.53	F[c]	6.39[d]	4.25[d]	13.5	5.95[d]	84.7	1.98[d]
	0000	.33		10.6	F[c]	1.35[d]	7.67	.84	41.4	5.66[d]	3.72[d]	7.07	5.32[d]	24.3	6.44[d]
	0100	1.51	.61[d]		2.60[d]	1.01[d]	8.62	3.38	F[c]	2.34[d]	.98[d]	10.5	8.28[d]	12.2[d]	4.55[d]
	0200		.83[d]	9.16	.82[d]	2.96[d]	17.8	9.95	23.0	5.66[d]	5.52[d]	73.5	8.47[d]	1.68[d]	5.52[d]
	0300	.87	.68[d]	15.5	.80[d]	1.82[d]	1.43	59.5	119	F[c]	4.86[d]	4.86[d]	7.07[d]		4.12[d]
	0400	.92	1.14[d]	11.8	1.71[d]	5.37[d]	142	72.1	182	60.5	4.86[d]	59.5	6.63[d]	12.5	1.81[d]
	0500		1.24[d]	.52	.78[d]	1.62[d]	65.7	6.74	478	5.87[d]	5.65[d]	44.1	6.39[d]		1.22[d]
C_2HCl_3	2200	8.33		2.29	F[c]	6.44[d]	4.23	8.33	2.32	6.27[d]	2.31[d]	31.8	.38[d]		
	2300	12.4	.25[d]	1.42	1.32[d]	5.23[d]	10.3	10.4	F[c]	4.75[d]	1.61[d]	5.12	.24[d]	4.04	3.49[d]
	0000	6.10		9.45	F[c]	5.39[d]	9.91	7.06	1.71	7.06[d]	1.79[d]	4.94[d]	.04[d]	5.98	6.94[d]
	0100	9.82	.10[d]		2.50[d]	7.39[d]	9.91	10.1	F[c]	4.16[d]	1.87[d]	27.0	.34[d]	4.27	1.97[d]
	0200		.02[d]	1.39	1.88[d]	6.83[d]	9.14	7.68	8.08	5.88[d]	1.79[d]	5.94	9.18[d]	8.02	2.68[d]
	0300	8.91	.14[d]	7.43	2.49[d]	5.23[d]	5.79	3.99	2.21	F	2.96[d]		5.94[d]		2.79[d]
	0400	9.24	.02[d]	9.45	1.61[d]	5.02[d]	2.02	4.66	2.28	5.21	1.61[d]	6.85	4.27[d]	3.81	5.82[d]
	0500		.06[d]	.41	3.16[d]	4.60[d]	2.30	13.7	2.88	1.37[d]	2.23[d]	6.75	6.94[d]		6.44[d]

See footnotes at end of table.

(continued)

TABLE 13 (continued)

Compound	Hour (CST)	Sampling Location[b]													
		8	9	11	5	6	7	18	15	14	13	12	10	20	19
C_2Cl_4	2200	1.80		1.46	F[c]	2.95[d]	4.20	3.18	3.22	2.48[d]	.69[d]	1.75	1.74[d]		
	2300	2.06	.60[d]	1.58	.70[d]	3.79[d]	3.28	1.32	F[c]	2.11[d]	1.26[d]	4.24		2.43	.70[d]
	0000	2.78		3.32	F[c]	3.41[d]	1.61	3.32	1.51	2.20[d]	1.00[d]	.12	2.57[d]	2.14	2.70[d]
	0100	1.63	.41[d]		.92[d]	1.65[d]	.32	3.14	F[c]	2.49[d]	.56[d]	2.82[d]	6.25[d]	1.97	.92[d]
	0200		.79[d]	1.56	.62[d]	2.11[d]	1.83	20.9	2.16	1.57[d]	.65[d]	3.98	2.37[d]	2.15	.96[d]
	0300	1.58	1.46[d]	1.98	.75[d]	2.11[d]	1.47	3.96	3.05	F[c]	.98[d]		2.38[d]	15600[d]	.95[d]
	0400	2.88	.55[d]	3.17	.72[d]	2.16[d]	4.20	3.91	5.61	7.09	2.13[d]	9.10	2.02[d]	1.45	1.52[d]
	0500		.83[d]	.75	.52[d]	2.63[d]	1.38	.01[d]	9.73	5.15[d]	5.45[d]	6.92	2.85[d]		2.38[d]
$C_2H_3Cl_3$	2200	68.5		2.99	F[c]	5.73[d]	0.0	3.36	5.33						
	2300	7.17		7.64	2.74[d]	10.6[d]	11.3		5.05			4.35		15.3	
	0000	7.00		11.8	F[c]	9.14[d]	7.52	5.52	4.16			6.51		17.7	
	0100	6.91			10.9[d]	9.04[d]	8.16	5.18	F[c]			7.83		11.7	
	0200			7.81	6.19[d]		7.47	5.02	6.80			7.60		20.0	
	0300	5.55		16.7	5.00[d]		5.39	5.05	4.46						
	0400	5.51		6.58			5.90	4.73	7.39	7.17		7.96		7.48	
	0500			4.42			5.27	9.79	14.9			7.92			

[a]Concentrations expressed in $\mu g\ m^{-3}$.

[b]See Figure 9 for sampling locations.

[c]F = flat bag.

[d]Peak height measurements.

SECTION 6

INTERPRETATION OF RESULTS

GENERAL APPROACH

For reasons that were alluded to earlier, not all the data were suitable for estimating emission rates. Frequently, the alignment of the tracer release line and the wind were not as they should have been. Sometimes there were too few valid samples. Flat bags, GC traces suitable for peak height analysis but not for peak area analysis, concentrations too low to be reliably estimated, and uncertainties regarding background concentrations all contributed to making many of the cases unsuitable for complete analysis. However, it was possible to identify five 1-hour test periods for which data could be used to estimate emission rates. These five periods are:

(1) 11 August 1981, 0000-0100 CST

(2) 11 August 1981, 0100-0200 CST

(3) 11 August 1981, 2200-2300 CST

(4) 12 August 1981, 2300-2400 CST

(5) 13 August 1981, 0400-0500 CST.

For each case, the concentration data (excluding those obtained by peak height analysis) were plotted as a function of distance along the sampling line. Smooth curves were drawn by hand to estimate the concentration distribution of each of the materials along this line. The lower concentrations near the ends of the line were taken to represent the background concentrations. In this way, it was possible to estimate the concentration contribution from the plant for each material believed to be emitted from the plant. Concentration distributions were estimated in the same way for SF_6. Estimates of the term B in Eq. (7) were derived from the data, using a value of 0.65 for b [from Eq. (2)] and estimates of distance to the upwind and downwind edges of the area source were based on the geometry of each test and the extent of the region where emissions were believed to be probable (as shown earlier in Figure 2). As noted earlier, the assumed area from which emissions took place was 2.5×10^4 m^2.

The same ratios of chlorinated hydrocarbon concentration to tracer concentration were used with Eq. (11) to obtain other estimates of the emission rates from the plant. The appropriate value of the term K in Eq. (11) was selected on the basis of meteorological observations.

ESTIMATED EMISSION RATES

11 August 1981, 0000-0100 CST

Figure 10 shows the concentrations observed at the various sampling locations for SF_6, CCl_4, C_2Cl_4, and C_2HCl_3. The measurements of $C_2H_3Cl_3$ were not sufficiently reliable on this day to be used to estimate the emission rates. The curves shown in Figure 10 were used to estimate the ratio of the peak concentration of the various compounds (above background) to that of the peak SF_6. These ratios are entered in the second column of Table 14.

Table 14 summarizes the values used for the various terms in order to estimate the emission rates of the three compounds for which reliable measurements were available. The last two columns are of greatest interest; they give the emission rates obtained from the area-source formulation (assuming a total area of 2.5×10^4 m^2) and from the point-source formulation. It is evident that in this case the two approaches for estimating total emission rates are quite consistent. The emission rates given are in g s^{-1}; 1 g s^{-1} is equal to 3.6 kg h^{-1}, so the emission rates given in Table 14 range from about 300 g h^{-1} to about 3 kg h^{-1}.

11 August 1981, 0100-0200 CST

Figure 11 shows the observed concentrations for the various compounds and the smooth curves that were drawn through the available points in order to estimate peak values. As before, ratios were determined between the observed peak concentrations of the chlorinated hydrocarbons and those of the tracer. These ratios are given in Table 15, which also summarizes the caluclations used to estimate the emission rates.

The last two columns in Table 15 show the estimated emission rates for the compounds. As was true before, the two approaches for estimating emission rates yield quite consistent results. However, this hour shows emission rates much higher than those estimated for the preceding hour. It appears that emission rates of about 20 to 25 kg h^{-1} were observed for C_2HCl_3 and CCl_4. This is a factor of 10 to 20 times those rates observed during the preceding hour. The apparent emission rates for C_2Cl_4 were also much higher during this hour than during the preceding hour. As will be seen from subsequent discussions, the lower values seem more typical, but similarly high estimates of CCl_4 emission rates were observed on at least one other occasion.

11 August 1981, 2200-2300 CST

Figure 12 shows the observed concentrations of three of the chlorinated hydrocarbons and that of the tracer. The concentrations of C_2HCl_3 were not above background, and it can be assumed that the emissions for this compound were quite low. The ratios determined from the graphs in Figure 12 are shown in Table 16.

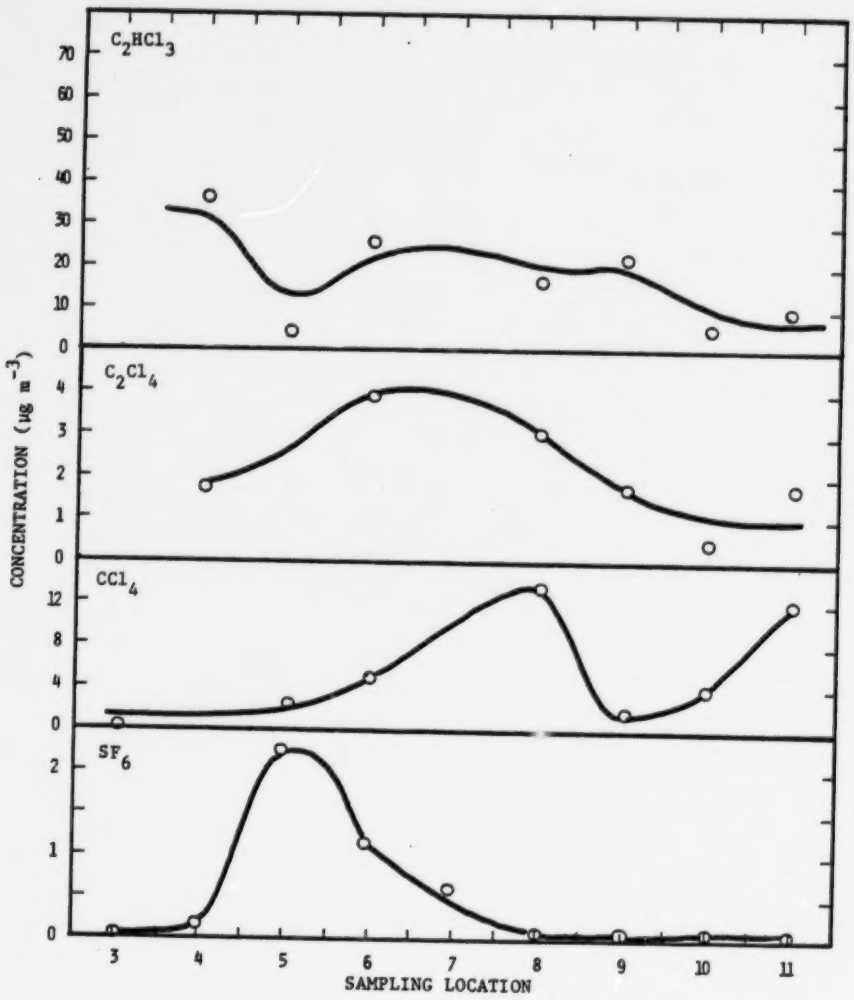

Figure 10. Concentrations on 11 August 1981, 0000-0100 CST.

TABLE 14. EMISSION RATE ESTIMATES FOR 11 AUGUST 1981, 0000-0100 CST

Compound	C_c/C_1	B in Equation 9	Q_1 ($g\ m^{-1}\ s^{-1}$)	$\frac{KQ_1X_p^{0.9}}{\sin\phi}$ in Equation 11	Estimated Emission Rates		
					Equation 9 ($g\ m^{-2}\ s^{-1}$)	Assuming area of $2.5 \times 10^4\ m^2$ ($g\ s^{-1}$)	Equation 11 ($g\ s^{-1}$)
CCl_4	5	10^{-2}	3.4×10^{-4}	6.7×10^{-2}	1.7×10^{-5}	0.4	0.3
C_2Cl_4	1	10^{-2}	3.4×10^{-4}	6.7×10^{-2}	3.4×10^{-6}	0.08	0.06
C_2HCl_3	9	10^{-2}	3.4×10^{-4}	6.7×10^{-2}	3.1×10^{-5}	0.8	0.6

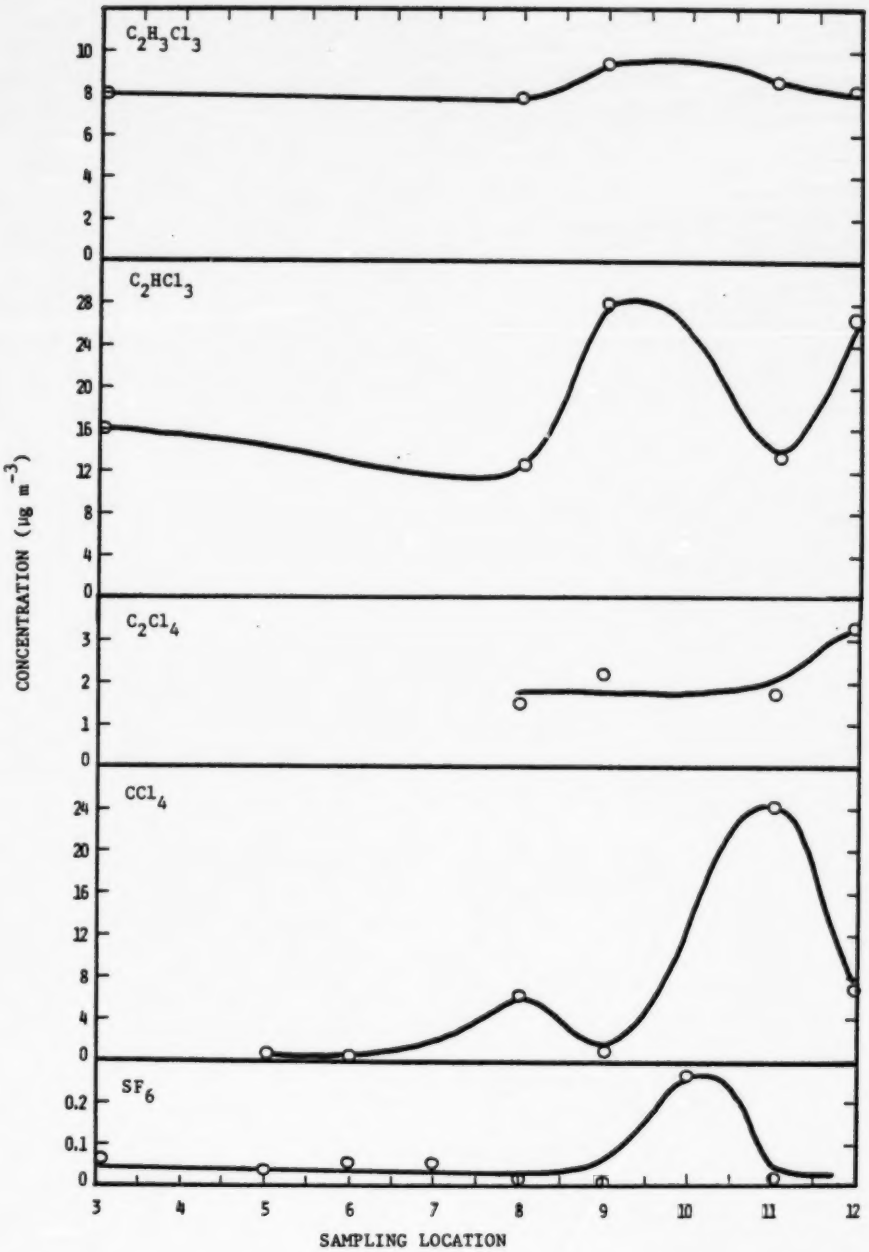

Figure 11. Concentrations on 11 August 1981, 0100-0200 CST.

TABLE 15. EMISSION RATE ESTIMATES FOR 11 AUGUST 1981, 0100-0200 CST

Compound	C_c/C_1	B in Equation 9	Q_1 ($g\ m^{-1}\ s^{-1}$)	$\frac{KQ_1X_p^{0.9}}{\sin\Phi}$ in Equation 11	Estimated Emission Rates		
					Equation 9 ($g\ m^{-2}\ s^{-1}$)	Assuming area of $2.5 \times 10^4\ m^2$ ($g\ s^{-1}$)	Equation 11 ($g\ s^{-1}$)
CCl_4	90	10^{-2}	3.4×10^{-4}	6.7×10^{-2}	3.1×10^{-4}	8	6
C_2Cl_4	7.5	10^{-2}	3.4×10^{-4}	6.7×10^{-2}	2.6×10^{-5}	0.6	0.5
C_2HCl_3	70	10^{-2}	3.4×10^{-4}	6.7×10^{-2}	2.4×10^{-4}	6	5
$C_2H_3Cl_3$	7	10^{-2}	3.4×10^{-4}	6.7×10^{-2}	2.4×10^{-5}	0.6	0.5

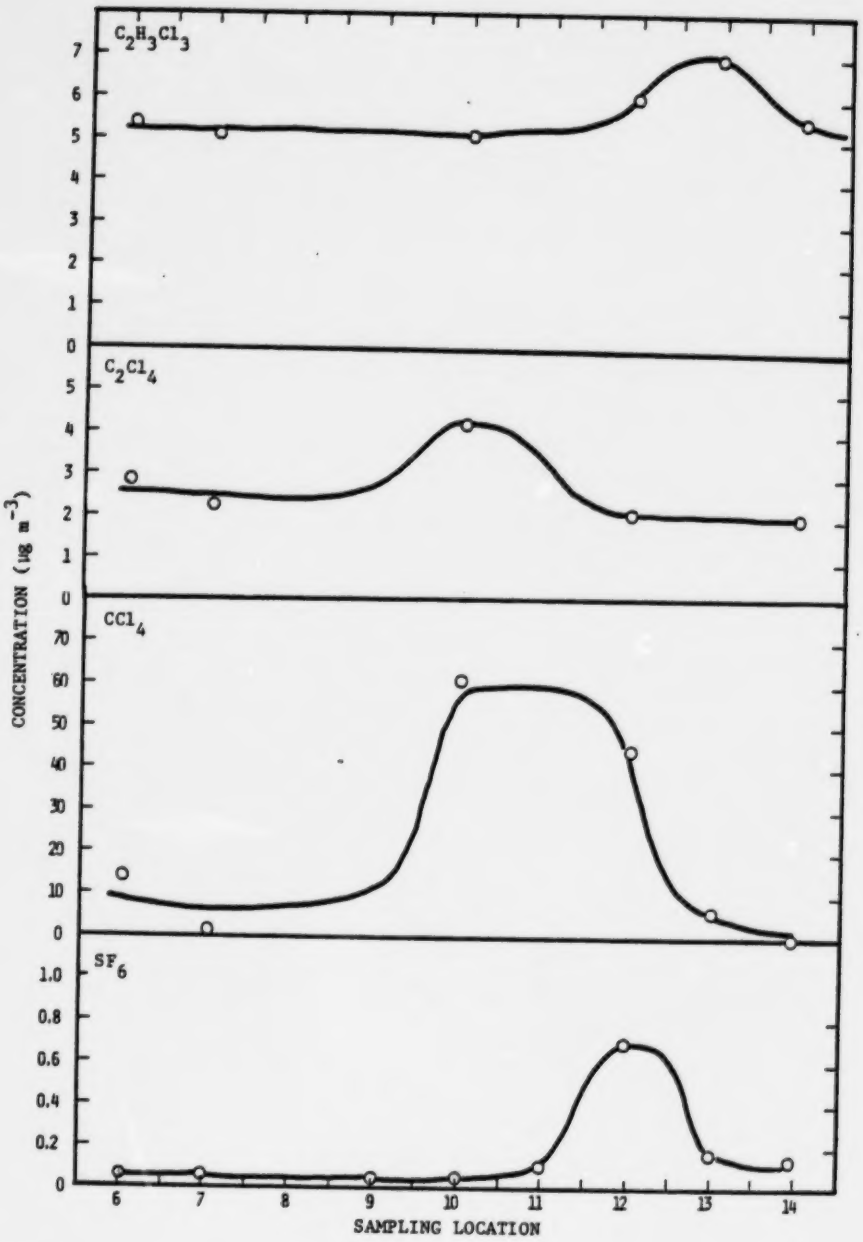

Figure 12. Concentrations on 11 August 1981, 2200-2300 CST.

TABLE 16. EMISSION RATE ESTIMATES FOR 11 AUGUST 1981, 2200-2300 CST

Compound	C_c/C_1	B in Equation 9	Q_1 ($g\ m^{-1}\ s^{-1}$)	$\frac{KQ_1X_p^{0.9}}{\sin\Phi}$ in Equation 11	Estimated Emission Rates		
					Equation 9 ($g\ m^{-2}\ s^{-1}$)	Assuming area of $2.5 \times 10^4\ m^2$ ($g\ s^{-1}$)	Equation 11 ($g\ s^{-1}$)
CCl_4	85	10^{-2}	2.6×10^{-4}	5.2×10^{-2}	2.2×10^{-4}	6	4
C_2Cl_4	2.7	10^{-2}	2.6×10^{-4}	5.2×10^{-2}	7.0×10^{-6}	0.2	0.1
$C_2H_3Cl_3$	2.7	10^{-2}	2.6×10^{-4}	5.2×10^{-2}	7.0×10^{-6}	0.2	0.1

The estimated emission rates are shown in the last columns of the table. Again, the estimates made by the two approaches are in reasonable agreement. The apparent emissions for this hour were somewhat smaller than those for the last hour discussed, 0100-0200 CST. The estimated CCl_4 emissions were about 20 kg h^{-1}, and those of the other two compounds were about 0.5 kg h^{-1}.

12 August 1981, 2300-2400 CST

Figure 13 shows the observed concentrations of the chlorinated hydrocarbons and the tracer, and the estimated distribution of these concentrations along the sampling line. The ratios shown in the second column of Table 17 were derived from the estimated peak concentrations of the various compounds.

The last two columns of Table 17 show the estimated emission rates obtained by the two approaches discussed in this report. The agreement in this case is much poorer than it was in the preceding case. Furthermore, the estimate derived from a point-source approximation is greater than the estimate derived from the area-source approximation; in the three preceding cases, the area-source approximation yielded larger estimates. During this test, the angle of the wind to the line-source release was only about 20^{o} or 30^{o}, a fact that may have contributed to the observed discrepancy between the two approaches. As noted before, a release more nearly normal to the wind direction better satisfies the approximations made in the derivation of the equations.

13 August 1981, 0400-0500 CST

This was the last case that was suitable for estimating emission rates. It suffered from the same shortcomings with regard to the angle between the wind direction and the line source as did the case for 12 August, 2300-2400 CST. Figure 14 shows the observed concentrations of the chlorinated hydrocarbons and the tracer, along with the smooth curves that were used for estimating the ratios shown in Table 18.

As was the case for 12 August, the estimates derived from the area-source and the point-source approximations do not agree very well. (See the last two columns of Tables 17 and 18.) Again, the estimate based on the point-source assumption is greater than the estimate based on the area-source assumption. The two results differ by about a factor of 3. The estimate based on Eq. (11) indicates that the emissions of CCl_4 were about 5 kg h^{-1}; the estimate based on Eq. (9) indicates the emissions were about 2 kg h^{-1}. The Eq. (11) estimates for the other compounds range from about 100 g h^{-1} for C_2HCl_3 to about 700 g h^{-1} for $C_2H_3Cl_3$. As noted before, the estimates with Eq. (1) are about one-third those from the other equations.

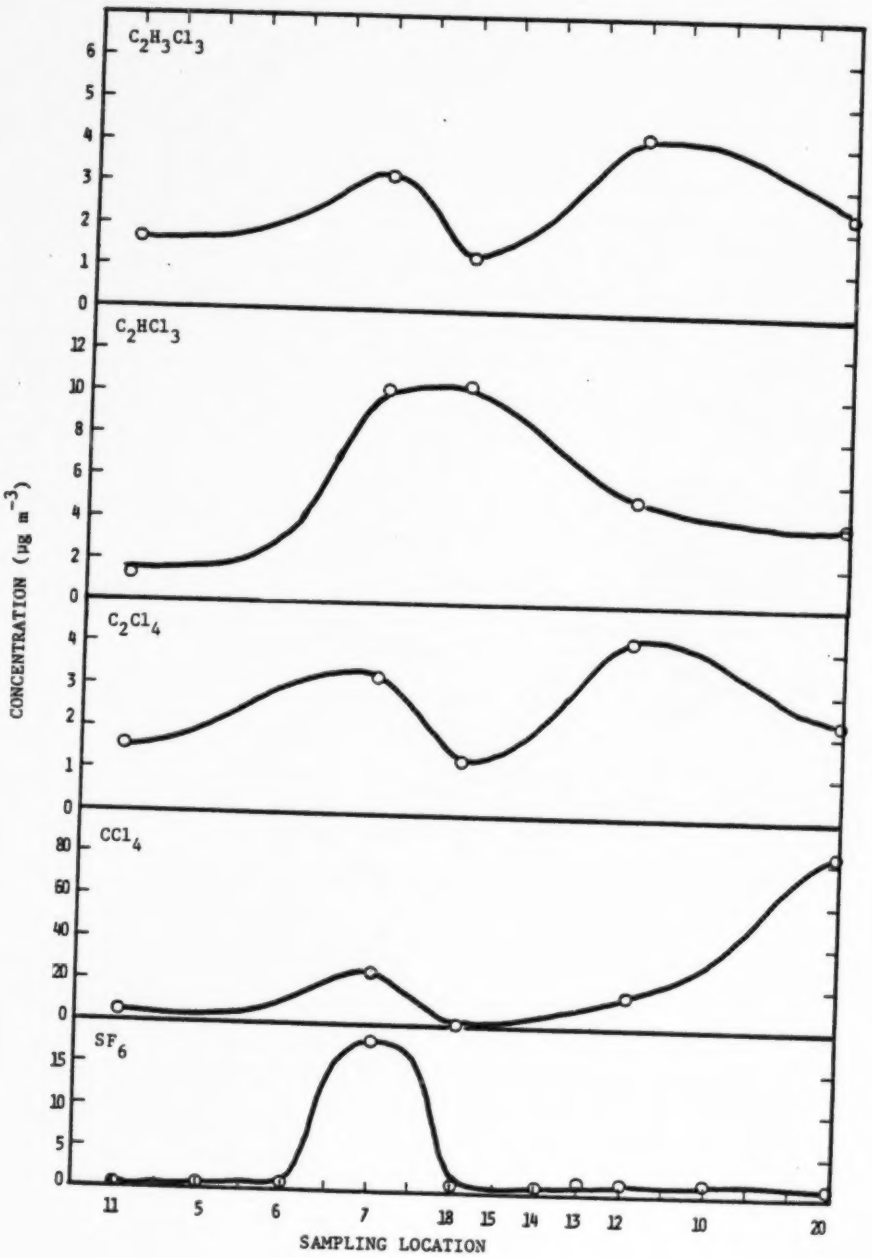

Figure 13. Concentrations on 11 August 1981, 2300-2400 CST.

TABLE 17. EMISSION RATE ESTIMATES FOR 12 AUGUST 1981, 2300-2400 CST

Compound	C_c/C_1	B in Equation 9	Q_1 ($g\ m^{-1}\ s^{-1}$)	$\frac{KQ_1X_p^{0.9}}{\sin\Phi}$ in Equation 11	Estimated Emission Rates		
					Equation 9 ($g\ m^{-2}\ s^{-1}$)	Assuming area of $2.5 \times 10^4\ m^2$ ($g\ s^{-1}$)	Equation 11 ($g\ s^{-1}$)
CCl_4	1	5.1×10^{-3}	2.9×10^{-4}	0.1	1.5×10^{-6}	0.04	0.1
C_2Cl_4	0.1	5.1×10^{-3}	2.9×10^{-4}	0.1	1.5×10^{-7}	0.004	0.01
C_2HCl_3	0.4	5.1×10^{-3}	2.9×10^{-4}	0.1	5.9×10^{-7}	0.01	0.04
$C_2H_3Cl_3$	0.1	5.1×10^{-3}	2.9×10^{-4}	0.1	1.5×10^{-7}	0.004	0.01

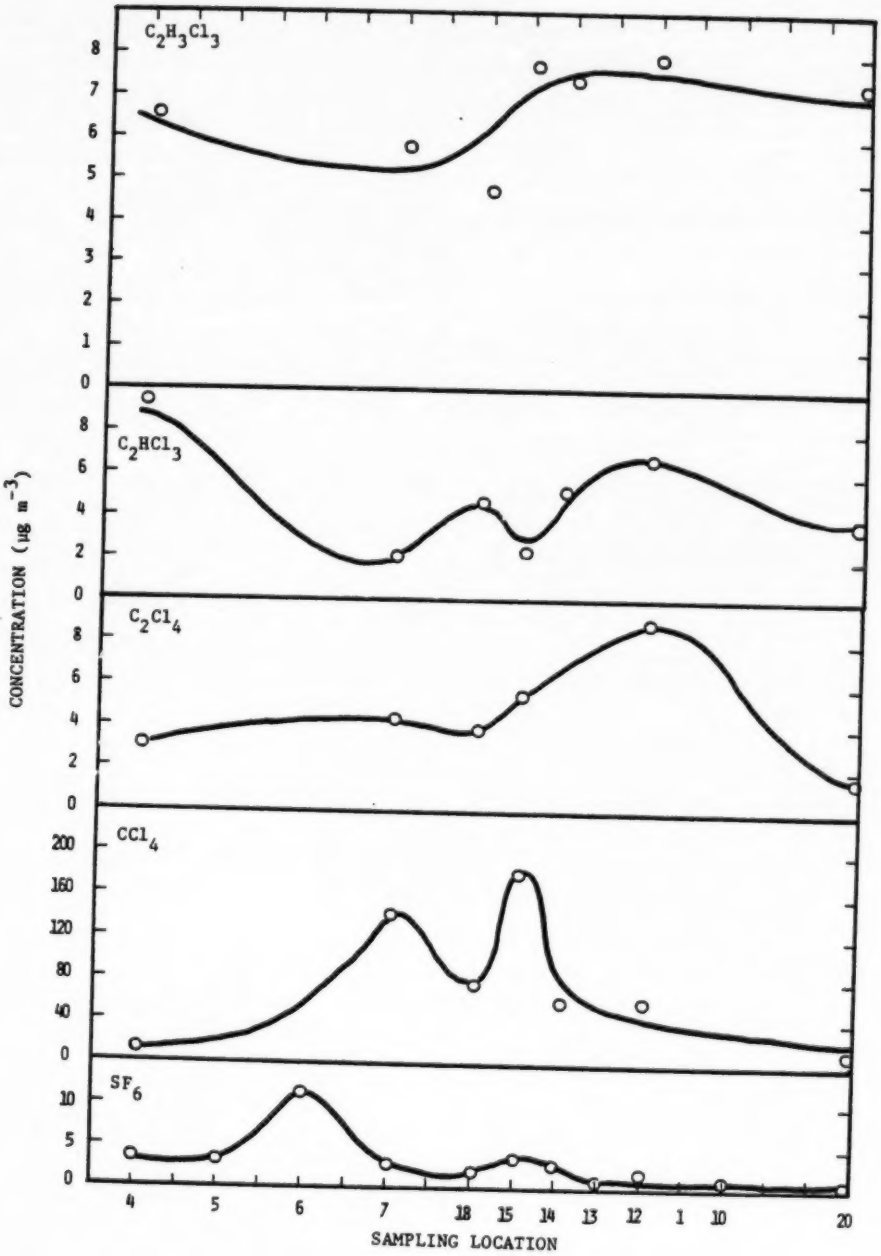

Figure 14. Concentrations on 13 August 1981, 0400-0500 CST.

TABLE 18. EMISSION RATE ESTIMATES FOR 13 AUGUST 1981, 0400-0500 CST

Compound	C_c/C_1	B in Equation 9	Q_1 ($g\ m^{-1}\ s^{-1}$)	$\frac{KQ_1X_p^{0.9}}{\sin\Phi}$ in Equation 11	Estimated Emission Rates		
					Equation 9 ($g\ m^{-2}\ s^{-1}$)	Assuming area of $2.5 \times 10^4\ m^2$ ($g\ s^{-1}$)	Equation 11 ($g\ s^{-1}$)
CCl_4	15	5.1×10^{-3}	2.9×10^{-4}	0.1	2.2×10^{-5}	0.6	1.5
C_2Cl_4	0.6	5.1×10^{-3}	2.9×10^{-4}	0.1	8.8×10^{-7}	0.02	0.06
C_2HCl_3	0.3	5.1×10^{-3}	2.9×10^{-4}	0.1	4.4×10^{-7}	0.01	0.03
$C_2H_3Cl_3$	2	5.1×10^{-3}	2.9×10^{-4}	0.1	3.4×10^{-6}	0.09	0.2

SECTION 7

SUMMARY AND RECOMMENDATIONS

ESTIMATED EMISSIONS

Table 19 summarizes the estimated emissions rates described in the preceding sections. It is immediately apparent from the table that the emission rates vary by more than two orders of magnitude. For the kinds of emissions that were measured, this does not seem unreasonable. Probably, the most frequently observed emissions would be comparable to those in the "minimum" columns of Table 19. It appears that some sporadic activities raise the emission rates appreciably for relatively short periods of time. It is not hard to imagine activities that could contribute to such elevated emissions: Drum filling, loading and unloading of containers, and other material transfer operations come immediately to mind.

SUGGESTED IMPROVEMENTS IN THE METHODOLOGY

The results obtained during this initial effort indicate that the methodology that has been developed has considerable promise, but that this first application did not always achieve that promise. It is not surprising that the potential of the method was not fully exploited in this effort, and future efforts should be able to profit by the errors made during this study. The following paragraphs present some suggestions for future efforts, based on our experience with the data collected during this study.

First, samples should be collected with greater spatial and temporal resolution. The data collected during this program suggest considerable variability in the emission rate. This means that there may be relatively short-term "puffs" of materials that come from different parts of the operation at different times during the hour-long sampling period. More closely spaced samplers would provide the spatial resolution necessary to resolve any such small-scale emissions. The closer spacing would also permit better definition of the peaks. Frequently the data collected in this study defined a peak with only a few observations. Of course, this problem was compounded by the difficulties that were encountered in some of the chemical analyses.

Finer temporal resolution; i.e., samples collected over a shorter period of time, would provide the information necessary to determine the short-term peak concentrations and the variability of emission rates.

TABLE 19. SUMMARY OF EMISSION RATE ESTIMATES FOR VULCAN PLANT

Compound	Rates Based on Equation 9 ($kg\ h^{-1}$)			Rates Based on Equation 11 ($kg\ h^{-1}$)		
	Maximum	Minimum	Average	Maximum	Minimum	Average
CCl_4	30	0.1	11	20	0.4	9
C_2Cl_4	2	0.01	0.7	2	0.04	0.5
C_2HCl_3	20	0.04	6	20	0.1	5
$C_2H_3Cl_3$	2	0.01	0.7	2	0.04	0.7

For a line-source length comparable to that used in this study, it would be possible to get valid averages for time periods as short as about 10 min.

If the samples are collected at more closely spaced locations, then it will be very important to develop techniques to limit the number of samples that must be analyzed in order to reduce costs. This could be done in at least two different ways.

First, a screening technique could be developed. The SF_6 results were used to some extent during this study to decide which bags were to be analyzed for the chlorinated hydrocarbons. A rapid, inexpensive method sensitive to chlorinated hydrocarbons might improve the screening process even further. Another approach to reducing the number of samples would be to limit the extent of the sampling line itself. The results of this study have shown that the emissions and the tracer affect only a limited length of the total sampling line at a given hour. The problem, of course, is to determine ahead of time just where the effects will be felt or to make appropriate adjustments during the sampling operation. SRI recommends that as much use as possible be made of U.S. National Weather Service forecasts. Accurate forecasts of changes in wind direction would allow each field test to be planned in such a way that the samplers could be moved during the course of a test if necessary. On-site wind-direction observations are an obvious necessity. An attempt was made during this study to change the sampling array following changes in wind direction, but no plans for changes in deployment were formulated ahead of time, based on forecasted wind-direction changes. Any redeployment of samplers could probably be carried out more effectively if it were planned ahead of time, using U.S. National Weather Service forecasts.

It should be noted that redeployment of samplers will introduce difficulties. Some data will be lost while samplers are being moved from place to place, but prior planning should reduce these losses. Serious complications will arise if records are not kept of the sampler locations at all times during a test. Careful bookkeeping with regard to sampler location will be absolutely essential. Again, prior planning based on weather forecasts should facilitate that bookkeeping

There may be diurnal patterns of activity in a plant, so that data collected at night could be unrepresentative. Therefore, future tests should include daytime measurements. The methodology described in this report emphasized its application at night, but the method can be applied in the daytime as well. The best approach would be to apply the methodology only during periods of neutral atmospheric stability. Such stability conditions occur when skies are overcast, day or night. The techniques and equations described in this report could be applied in the daytime under neutral conditions. If tests were undertaken during periods of instability, it would be necessary to revise the equations. It is our recommendation that daytime applications of the method be limited to conditions of overcast skies with light winds.

The patterns of activity mentioned in the preceding paragraph could provide useful clues regarding specific sources of observed chlorinated hydrocarbon concentrations downwind of a plant. The plant studied in this program is arranged so that it is impossible to observe and record events at the plant from outside and the lack of such information has proved to be unfortunate. Such information might have provided reasons for the observed emission variability. At sites where it is possible, it would be desirable to have an observer recording information about:

(1) Truck arrivals and departures

(2) Movements of railroad tank cars

(3) Outdoor drum-filling operations that might be visible

(4) Changes in the visible emissions from the plant complex.

Such information is sometimes subjective and almost always difficult to incorporate into an automated data processing system, but as noted earlier, it can be very valuable to the interpretation of observed concentrations.

The original intent in developing this methodology was to release the tracer from within the plant complex by using some sort of extended manifold or multiple sources to simulate the areal extent of the fugitive sources. For reasons noted in Section 1, it was not possible to do this. However, SRI still believes that that approach would introduce the fewest uncertainties and would provide the most reliable results. Whenever it is possible to release tracers collocated with the sources of interest, the experiment should be conducted that way.

In summary, the methodology described in this report has been demonstrated to be workable, although it still needs improvement. The method has already provided some interesting estimates of emissions from a chlorinated hydrocarbon plant, by using only measurements made outside the plant area. If the recommended improvements are instituted, future programs using this methodology could provide even better estimates of emission rates.

REFERENCES

1. Busse, A.D., and J.R. Zimmerman. Users Guide for the Climatological Dispersion Model. R4-73-024, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1973. 144 pp.

2. Turner, D.B. Workbook of Atmospheric Dispersion Estimates. 999-AP-26, Public Health Service, Cincinnati, Ohio, 1970. 84 pp.